

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of Andrew McIntosh Soutar et al. Art Unit 1762
Serial No. 10/099,936
Filed March 13, 2002
Confirmation No. 3281
For SOLDERABILITY ENHANCEMENT BY SILVER IMMERSION PRINTED
 CIRCUIT BOARD MANUFACTURE
Examiner Brian K. Talbot

July 2, 2007

THIRD AMENDED APPEAL BRIEF

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This is the third amended appeal from the final rejection of the claims of the above-referenced application made in the Office action dated October 6, 2005. This third amended appeal brief is filed in response to the Notification of Non-Compliant Appeal Brief dated May 1, 2007. A Notice of Appeal was filed on April 3, 2006.

I. REAL PARTY IN INTEREST

The real party in interest is Enthone Inc., a corporation of the State of Delaware, owner of a 100 percent interest in the pending application.

II. RELATED APPEALS AND INTERFERENCES

Appellants are unaware of any pending appeals or interferences which may be related to, directly affect or be directly affected by, or have a bearing on, the Board's decision in the pending appeal.

III. STATUS OF CLAIMS

The following is a statement of the status of all claims:
Claims 1-17. Canceled.
Claims 18-26. Rejected.
Claims 27-31. Canceled.

Claims 32-40. Rejected.

The claims being appealed are claims 18-26 and 32-40.

A copy of the pending claims 18-26 and 32-40 appears in the Claims Appendix of this Brief.

The pending claims stand rejected under 35 U.S.C. §112 on the basis of the examiner's assertion that there is not support in the original disclosure for "fatty amides" which is an element of all of claims 18-26 and 32-40. It is also asserted that the original disclosure lacks support for "oxidant" which appears in claims 20, 23, 26, 34, 37, and 40.

The rejections of all of these claims are being appealed.

IV. STATUS OF AMENDMENTS

No amendments have been filed after the final rejection.

V. SUMMARY OF CLAIMED SUBJECT MATTER

The following is a concise explanation of the subject matter defined in each of the independent claims (18, 24, 32, 38) involved in the appeal, referring to the specification by page and line number (there are no drawings):

Claim 18: This claim is directed to a process for immersion plating of silver onto a metal surface by treating the surface with a solution (specification page 16 lines 19-23 and page 19, lines 20-22) comprising a) a soluble source of silver ions (specification page 14, line 12); b) an acid (specification page 24, lines 17-18, and 24-25); and c) an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, and ethoxylated versions of any of the foregoing (specification page 22, lines 10-15).

Claim 24: This claim is directed to a solution for immersion plating comprising i) a soluble source of silver ions (specification page 14, line 12); ii) an acid (specification page 24, lines 17-18, and 24-25); and iii) an additive selected from the group

consisting of fatty amines, fatty amides, quaternary salts, and ethoxylated versions of any of the foregoing (specification page 22, lines 10-15).

Claim 32: This claim is directed to process for improving solderability of a metal surface by contacting the surface with an immersion silver plating solution and thereafter treating the surface with a solution (specification page 16, lines 24-26) comprising an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, and ethoxylated versions of any of the foregoing (specification page 22, lines 10-15).

Claim 38: This claim is directed to an immersion silver plating solution comprising an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, and ethoxylated versions of any of the foregoing (specification page 22, lines 10-15).

The invention relates to plating of silver onto a metal surface to improve the solderability of the surface. The plating is achieved by so-called "immersion" plating which differs from electroplating because in immersion plating no external current is applied. The invention has special applicability to plating silver onto copper elements of printed circuit boards, to preserve their solderability for subsequent manufacturing operations.

Each of the independent claims in this application focuses on the specific tarnish inhibitors disclosed in paragraph [0072] of applicants' published application (2002/0150692), e.g.:

18. A process for improving the solderability of a metal surface, said process comprising treating the metal surface with an immersion silver plating solution, said solution comprising:

- a). a soluble source of silver ions;
- b). an acid;

c). an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, and ethoxylated versions of any of the foregoing.

The other independent claims are essentially the same with respect to the first salient issue on appeal -- whether "fatty amides" is supported by the original specification.

The second salient issue on appeal -- whether "oxidant" is supported by the specification -- is manifest in six of the dependent claims, e.g.:

20. A process according to claim 18 wherein the silver plating solution also comprises an oxidant.

The present application is a continuation of application 08/939,656, which is now U.S. Pat. 6,395,329. A parallel continuation issued as 6,860,925. A sample claim in 6,395,329 is as follows:

1. A method for coating a printed circuit board having metal pads, metal through-holes or a combination thereof, the metal pads, metal through-holes or the combination thereof being formed of a first metal, the method comprising the steps of:

contacting the metal pads, the metal through-holes or the combination thereof with a bright-etch composition to form etched pads, etched through-holes or a combination thereof, the etched pads, the etched through-holes or the combination thereof being formed of the first metal; and

contacting the etched pads, the etched through-holes or the combination thereof with a plating composition comprising ions of a second metal, the second metal being different from the first metal, and a tarnish inhibitor, the tarnish inhibitor characterized in that it coexists with the second metal in solution, to form a printed circuit board having pads, through-holes or a combination thereof that are formed of the first

metal coated by a separate layer of the second metal and by a layer of the tarnish inhibitor.

A sample claim in 6,860,925 is as follows:

1. A plating solution comprising: a solvent; metallic ions dissolved in the solvent; and a tarnish inhibitor in the solvent, the tarnish inhibitor characterized in that it does not cause the dissolved metallic ions to precipitate in the solution.

VI. GROUND OF REJECTION TO BE REVIEWED ON APPEAL

The issue under appeal is whether the subject matter of claims 18-26 and 32-40 satisfy the requirements of 35 U.S.C. §112, first paragraph. Accordingly:

Appellants appeal the rejection of claims 18-26 and 32-40 under 35 U.S.C. §112, first paragraph for failing to comply with the written description requirement.

VII. ARGUMENT

Briefly, The Office has taken the positions that: (1) there is no support in the original specification for the term "fatty amides" in claims 18, 24, 32, and 38; and (2) there is no support in the original specification for the term "oxidant" in dependent claims 20, 23, 26, 34, 37, and 40. All 18 pending claims require "fatty amides," but only six pending claims require "oxidant." Accordingly, arguments presented below with regard to claims 18-19, 21-22, 24-25, 32-33, 35-36, and 38-39 pertain to the rejection based on the Office's assertion that the original disclosure lacks support for "fatty amides." Further, arguments presented below with regard to claims 20, 23, 26, 34, 37, and 40 pertain to the rejection based on the Office's assertion that the original disclosure lacks support for "oxidant" and "fatty amides."

A. Claims 18, 19, 21, 22, 24, 25, 32, 33, 35, 36, 38, and 39

These claims recite "fatty amides" but do not recite "oxidant," so the only rejection basis relevant to these claims is whether there is support in the original specification for "fatty amides." Written description support for "fatty amides" is found at page 22, line 13 [Paragraph 0072 of published application No. US 2002/0150692]:

"(a) fatty acid amines, preferably having at least 6 carbon atoms, most preferably at least 10 carbon atoms and generally no greater than 30 carbon atoms, they may be primary, secondary, tertiary, diamines, amine salts, amides, ethoxylated amines, ethoxylated diamines, quaternary ammonium salts, quaternary diammonium salts, ethoxylated quaternary ammonium salts, ethoxylated amides and amine oxides. Examples of the primary, secondary and tertiary amine type corrosion inhibitors are ARMEEN™ to (™ denotes trademark). Examples of the subsequent amine type corrosion inhibitors are respectively DUOMEEN™, ARMAC™/DUOMAC, ARMID™, ETHOMEEN™, ETHODUONEEN™, ARQUAD™, DUOQUAD™, ETHOQUAD™, ETHOMID™, AROMOX™, all supplied by Akzo Chemie." (Emphasis added.)

This same paragraph appears in the priority application, now 6,395,329, at column 10, line 10 ff, and at page 22, line 10 ff of the originally filed applications -- both present application 10/099,936, and 08/839,656 which matured into 6,395,329.

This paragraph states "they may be ... amides" "They" clearly refers back to the "fatty acid amines." So the "amides" linked to the "fatty acid amines" by "they" must also be "fatty." An amide is, by definition, "a product of a reaction between a carboxylic acid and an amine." If an amine is "fatty," its corresponding amide must also be "fatty." That is, the reaction from an amine to an amide does not destroy the

compound's long hydrocarbon chain, so the corresponding amide compound is also "fatty."

Accordingly, one skilled in the art would understand "amides" at page 22, line 13 to be referring to amides which are, in fact, fatty, such that "fatty amides" is supported literally. And, in particular, one would understand applicants to have been in possession of the invention comprising silver plating with a composition comprising among other components, fatty amides, for solderability enhancement.

Moreover, even if the cited passage of the specification were deemed to fall short of literal support, claim language is supported if the disclosure "reasonably conveys to the artisan that the inventor had possession at that time of the later claimed subject matter." *Lampi Corp. v. American Power Products Inc.*, 56 USPQ2d 1445, 1455 (Fed. Cir. 2000). It is not necessary that the claim language such as "fatty amides" be supported in exact terms:

[W]e are mindful that appellant's specification need not describe the claimed invention in *ipsis verbis* to comply with the written description requirement. The test is whether the originally filed specification disclosure reasonably conveys to a person having ordinary skill that applicant had possession of the subject matter later claimed. *In re Sorenson*, 3 USPQ2d 1462, 1463 (BPAI 1987).

The claim language under scrutiny in *Sorenson* included "copper complexes of imines," "binuclear copper complexes of carboxylic acids," and "a binuclear copper complex of an aliphatic carboxylic acid or binuclear copper complex of an aryl carboxylic acid." *Sorenson*, 3 USPQ2d at 1463. The examiner in *Sorenson* acknowledged that the specification contained broader expressions that encompassed the claim language at issue, including "an organic compound of copper", "copper complexes of

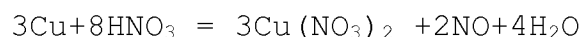
carboxylic acids," "copper complex of an aliphatic carboxylic acid," and the "copper complex of an aryl carboxylic acid]. The examiner nonetheless rejected the claims for failing to satisfy the written description requirement. The Board reversed and found that, although the specification did not use the exact language found in the claims, the disclosure as a whole reasonably conveyed to the skilled artisan that the applicant had possession of the claimed subject matter. *Id.* at 1463-64. Here, a skilled artisan reading the specification's disclosure of "fatty amines," which "may be...amides," would immediately recognize that applicants had possession of an immersion silver plating solution comprising a fatty amide additive. The written description requirement of Section 112 is satisfied.

B. Claims 20, 23, 26, 34, 37, and 40

These claims require "fatty amides" and "oxidant." There is support for "fatty amides" for the reasons stated immediately above. Also, written description support for "oxidant" is provided, for example, by the numerous references in the original specification to "nitric acid" as a component of the plating composition (E.g., paragraphs 0086, 0103, 0123, and 0125). Nitric acid is a known oxidant and a known oxidant for copper:

U.S. PAT. 4,846,918, Col. 1, lns 58-64

In the nitric acid etching chemistry disclosed in U.S. Pat. Nos. 4,497,687 and 4,545,850, nitric acid reacts with copper according to the relationship



with the **nitric acid serving both as an oxidant and as an anion source for the dissolved copper.**

U.S. PAT. 5,362,712; Claim 1

1. . . . to dissolve the copper mold . . . **nitric acid is simultaneously used as said mineral acid and said oxidizing agent**

U.S. PAT. 5,037,482; Col. 5, lns 23 ff.

The oxidizer must be of a type, and present in an amount, sufficient to provide in cooperating interaction with the surfactant, a controlled conversion of the copper surface from a substantially smooth surface to a substantially clean, substantially uniformly micro-roughened surface, so that the bonding characteristics of the copper surface are substantially increased for securely adhering a subsequently applied coating to the copper surface, without at the same time removing the copper surface itself from the underlying substrate to which it is adhered. An oxidizing agent which is too active, and/or which is used in too substantial concentrations, not only runs the risk of uncontrolled stripping of the copper surface from its underlying substrate, but more importantly has been found ineffective to produce the required micro-roughened topography on the remaining **copper surface. Results such as this have been found with compositions containing nitric acid as the oxidizer.** Even where complete stripping is avoided, the remaining copper surface is nevertheless surprisingly smooth and unacceptable for promoting adhesion of subsequently applied coatings. [Nitric acid was discussed in the context of the prior art; and the inventors preferred methane sulfonic acid over nitric acid.]

Nitric acid in the context of these solutions is well understood to provide nitrate ions which facilitate oxidization of Cu to Cu^{+1} and/or Cu^{+2} by the most basic of chemical re-dox reactions.

In light of the state of the knowledge in the art, the specification's disclosure of "nitric acid" – a known oxidant for copper – reasonably conveys to the artisan that applicants had possession of immersion silver plating solutions comprising

an oxidant. Therefore, the written description requirement of Section 112 is satisfied.

C. THE OFFICE HAS NOT MADE A *PRIMA FACIE* SHOWING

Because the written description requirement does not require in *ipsis verbis* support in the specification, the Office bears "the initial burden of presenting evidence or reasons why persons skilled in the art would not recognize in the disclosure a description of the invention defined by the claims." *In re Wertheim*, 191 USPQ 90, 97 (CCPA 1976); *In re Alton*, 37 USPQ2d 1578, 1583 (Fed. Cir. 1996).

The *Wertheim* court found that the Patent Office did "nothing more than to argue lack of literal support." *Wertheim*, 191 USPQ at 98. The court found this inadequate:

If lack of literal support alone were enough to support a rejection under § 112, then the statement of *In re Lukach* that "the invention claimed does not have to be described in *ipsis verbis* in order to satisfy the description requirement of § 112," is empty verbiage. *Id.* (citations omitted).

Here, the Office has not provided sufficient evidence or reasoning for concluding that the written description requirement is not satisfied for "fatty amides" or "oxidant." More importantly, the disclosure "reasonably conveys to a person having ordinary skill that applicant had possession of the subject matter later claimed," i.e., of silver plating using compositions containing fatty amides and an oxidant to improve solderability.

D. Conclusion

Claims 18, 19, 21, 22, 24, 25, 32, 33, 35, 36, 38, and 39 should be allowed because there is adequate support in the specification for the term "fatty amides." Claims 20, 23, 26, 34, 37, and 40 should be allowed because there is adequate support in the specification for "oxidant" and "fatty amides." Appellants therefore respectfully request the rejections be reversed and these two groups of pending claims be allowed.

Respectfully submitted,

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VIII. CLAIMS APPENDIX

Rejected claims under appeal: 18-26, 32-40.

1. (Canceled) A method for coating a printed circuit board comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising contacting the pads and/or through-holes with a bright-etch composition in a bright-etch step; and subsequently metal plating the etched pads and/or through-holes by contact with a plating composition comprising ions of a metal which is more electropositive than the metal from which the pads and/or through-holes are formed and being substantially free of reducing agent for said ions in an immersion metal plating step to form solderable plated metal surfaces.

2. (Canceled) A method according to claim 1 in which the plated metal surfaces are contacted with a solution of a tarnish inhibitor.

3. (Canceled) A method for coating a printed circuit board comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising metal plating the etched pads and/or through-holes by contact with a plating composition in a metal plating step to form solderable plated metal surfaces and contacting the plated metal surfaces with a solution of tarnish inhibitor.

4. (Canceled) A method according to claim 1 in which the metal plating step is a method in which a metal which is more

electropositive than the metal of the said pads and/or through-holes is immersion/displacement coated from an aqueous solution containing ions of the more electropositive metal substantially free of reducing agent for said ions.

5. (Canceled) A method according to claim 1 in which the plating composition contains a complexing agent for the said ions, preferably a multidentate ligand complexing agent.

6. (Canceled) A method according to claim 1 or claim 3 in which the plating composition comprises a tarnish inhibitor and in the process, the metal surfaces are contacted with a solution comprising a tarnish inhibitor during the plating step, so that the tarnish inhibitor is present in the metal plating composition.

7. (Canceled) A method according to claim 1 or claim 3 in which the metal plated surfaces are formed in the plating step and subsequently the pre-formed plated metal surfaces are contacted with a solution comprising a tarnish inhibitor in a postrinse second step.

8. (Canceled) A method according to claim 2 or claim 3 in which the contact time of the plated metal surfaces with the solution comprising a tarnish inhibitor is from 10 seconds to 5 minutes.

9. (Canceled) A method according to claim 2 or claim 3 in which the metal surfaces are contacted with a solution comprising a tarnish inhibitor by dip coating or spray coating.

10. (Canceled) A method according to claim 2 or claim 3 in which the tarnish inhibitor is present in the solution in an amount of from 0.001 to 5% by weight of the solution.

11. (Canceled) A method according to claim 1 in which the metal coating of the plated metal surfaces comprise nickel, silver, tin, lead, palladium, cobalt, gold, platinum or bismuth or their alloys, preferably silver.

12. (Canceled) A method according to claim 1 in which the pads or through-holes are formed of copper.

13. (Canceled) A method according to claim 1 including a preliminary step of applying to exposed conductor traces at the surface of the PCB a mask which is an insulator, such that the pads and/or through-holes are left exposed.

14. (Canceled) A method according to claim 1 including a subsequent step of attaching conducting components to the metal plated pads and/or through-holes using solder in direct contact with the metal plating.

15. (Canceled) An aqueous plating composition suitable for forming an immersion plating of a relatively more electropositive metal on a relatively less electropositive metal substrate containing ions of the more electropositive metal and a complexing agent for the ions and a tarnish inhibitor for the more electropositive metal and being substantially free of reducing agent for said ions.

16. (Canceled) A composition according to claim 15 in which the tarnish inhibitor is present in the solution in an amount of from 0.001 to 5% by weight of the composition.

17. (Canceled) A composition according to claim 15 in which the said ions are of nickel, silver, tin, lead, palladium, cobalt, gold, platinum or bismuth or their alloys, preferably silver.

18. (Rejected) A process for improving the solderability of a metal surface, said process comprising treating the metal surface with an immersion silver plating solution, said solution comprising:

- a). a soluble source of silver ions;
- b). an acid;
- c). an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, and ethoxylated versions of any of the foregoing.

19. (Rejected) A process according to claim 18 wherein the silver plating solution also comprises material selected from the group consisting of imidazoles, benzimidazoles, imidazole derivatives and benzimidazole derivatives.

20. (Rejected) A process according to claim 18 wherein the silver plating solution also comprises an oxidant.

21. (Rejected) A process according to claim 18 wherein the metal surface comprises copper.

22. (Rejected) A process according to claim 21 wherein the silver plating solution also comprises a material selected from the group consisting of imidazoles, benzimidazoles, imidazole derivatives, and benzimidazole derivatives.

23. (Rejected) A process according to claim 22 wherein the silver plating solution also comprises an oxidant.

24. (Rejected) An immersion silver plating solution comprising

- (i) a soluble source of silver ions,
- (ii) an acid and
- (iii) an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, and ethoxylated versions of any of the foregoing.

25. (Rejected) An immersion plating solution according to claim 24 also comprising a material selected from the group consisting of imidazoles, benzimidazoles, imidazole derivatives, and benzimidazole derivatives.

26. (Rejected) An immersion plating solution according to claim 24 also comprising an oxidant.

27. (Canceled) A process for improving the solderability of a metal surface, said process comprising treating the metal surface with an immersion silver plating solution, said solution comprising:

- a). a soluble source of silver ions;
- b). an acid; and

c). an additive that substantially prevents silver migration by providing a barrier to moisture.

28. (Canceled) A process for improving the solderability of a metal surface, said process comprising:

a). contacting the metal surface with an immersion silver plating solution thereby producing an immersion silver plate upon the metal surface; and

b). treating the immersion silver plated metal surface with a solution comprising an additive that substantially prevents silver migration by providing a barrier to moisture.

29. (Canceled) A process according to claim 28, wherein the solution described in step (b) is distinct from the immersion plating solution of step (a), and step (b) is performed after step (a).

30. (Canceled) A process according to claim 28, wherein the additive is a component of the immersion silver plating solution.

31. (Canceled) An immersion silver plating solution comprising (i) a soluble source of silver ions, (ii) an acid and (iii) an additive that substantially prevents silver migration by providing a barrier to moisture.

32. (Rejected) A process for improving the solderability of a metal surface, said process comprising:

a). contacting the metal surface with an immersion silver plating solution thereby producing an immersion silver plate upon the metal surface; and thereafter

b). treating the immersion silver plated metal surface with a solution comprising an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, and ethoxylated versions of any of the foregoing.

33. (Rejected) A process according to claim 32 wherein the silver plating solution comprises a material selected from the group consisting of imidazoles, benzimidazoles, imidazole derivatives and benzimidazole derivatives.

34. (Rejected) A process according to claim 32 wherein the silver plating solution also comprises an oxidant.

35. (Rejected) A process according to claim 32 wherein the metal surface comprises copper.

36. (Rejected) A process according to claim 35 wherein the silver plating solution comprises a material selected from the group consisting of imidazoles, benzimidazoles, imidazole derivatives and benzimidazole derivatives.

37. (Rejected) A process according to claim 36 wherein the silver plating solution also comprises an oxidant.

38. (Rejected) An immersion silver plating solution comprising an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, and ethoxylated versions of any of the foregoing.

39. (Rejected) An immersion plating solution according to claim 38 also comprising a material selected from the group

consisting of imidazoles, benzimidazoles, imidazole derivatives, and benzimidazole derivatives.

40. (Rejected) An immersion plating solution according to claim 38 also comprising an oxidant.

IX. EVIDENCE APPENDIX

REFERENCES

U.S. Pat. 2002/0150692.....	3, 6
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X. RELATED PROCEEDINGS APPENDIX

There are no related appeals or interferences.



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Soutar et al. (43) **Pub. Date: Oct. 17, 2002**

(54) **PRINTED CIRCUIT BOARD MANUFACTURE**(30) **Foreign Application Priority Data**

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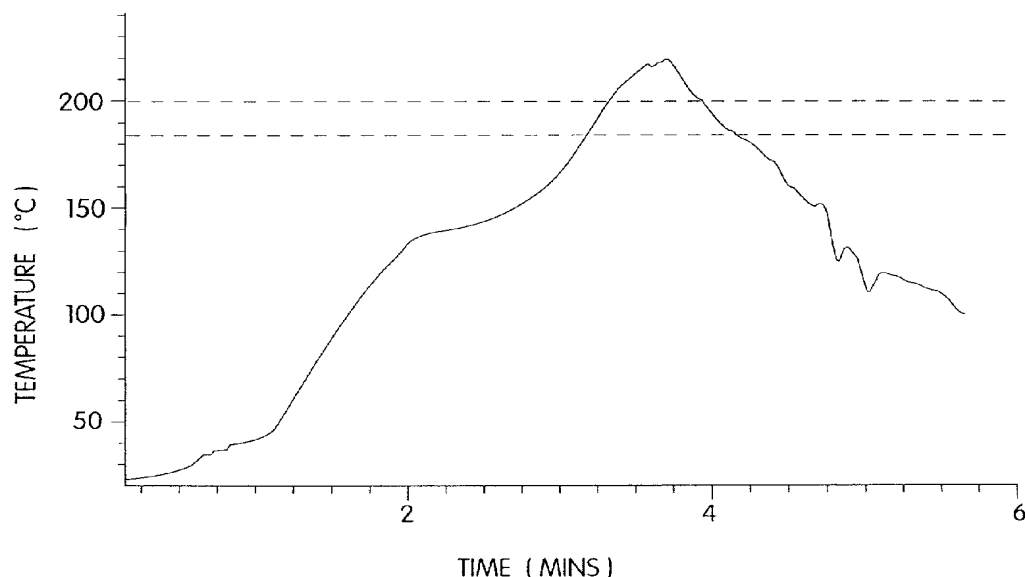
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106/1.24; 106/1.25; 106/1.26;
106/1.27; 106/1.28(21) Appl. No.: **10/099,936**(22) Filed: **Mar. 13, 2002****Related U.S. Application Data**

(63) Continuation of application No. 08/939,656, filed on
Sep. 29, 1997, now Pat. No. 6,395,329, which is a
continuation of application No. 08/567,885, filed on
Dec. 8, 1995, now abandoned.

(57) **ABSTRACT**

A process used during manufacture of printed circuit boards comprises protecting metal pads and/or through-holes to provide a tarnish-resistant and solderable coating. In the method, the pads and/or through-holes are bright-etched, metal plated, preferably by an immersion process, and treated with a tarnish inhibitor. The tarnish inhibitor may be incorporated into the immersion plating bath. The metal plating is usually with silver or bismuth and the pads and/or through-holes comprise copper.



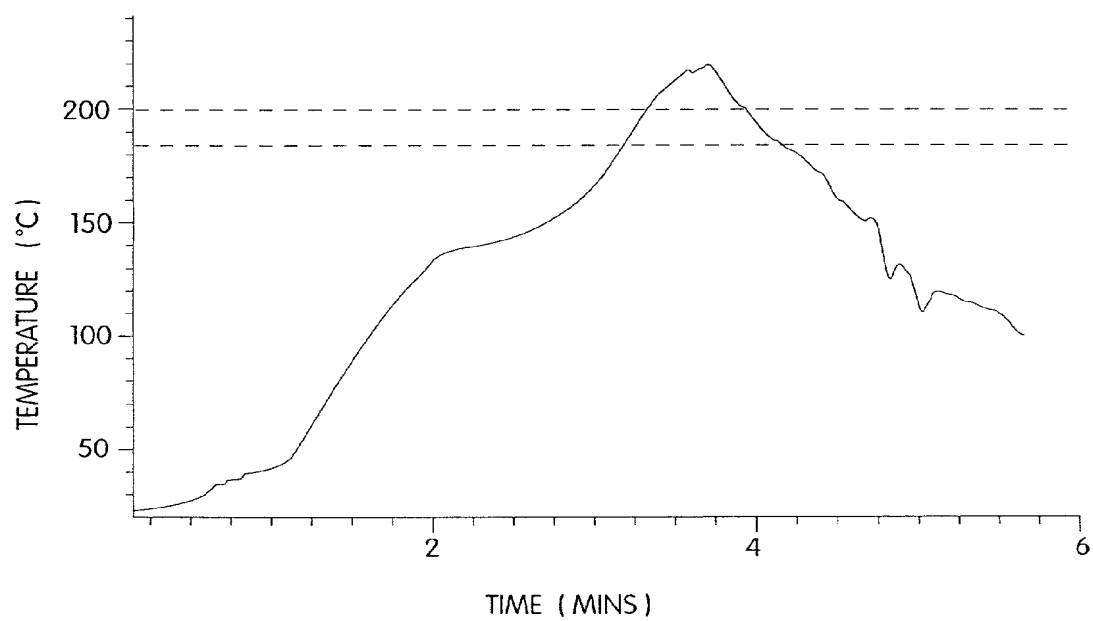


Fig. 1

PRINTED CIRCUIT BOARD MANUFACTURE

FIELD OF THE INVENTION

[0001] In the production of a printed circuit board (PCB), in a first (multi-step) stage a "bare board" is prepared and in a second (multi-step) stage, various components are mounted on the board. The present invention relates to the final steps in the manufacture of the bare board, in which the bare board is coated with a protective layer prior to passing to the second production stage.

PRIOR ART

[0002] There are currently two types of components for attachment to the bare boards in the second stage referred to above: legged components e.g. resistors, transistors, etc., and, more recently, surface mount devices. Legged components are attached to the board by passing each of the legs through a hole in the board and subsequently ensuring that the hole around the leg is filled with solder. Surface mount devices are attached to the surface of the board by soldering with a flat contact area or by adhesion using an adhesive.

[0003] In the first stage referred to above, a board comprising an insulating layer, a conducting circuit pattern and conductive pads and/or through-holes is produced. The board may be a multi-layer board having more than one conducting circuit pattern positioned between insulating layers or may comprise one insulating layer and one conducting circuit pattern.

[0004] The through-holes may be plated through so that they are electrically conducting and the pads which form the areas to which the surface mount components will be attached in the subsequent component-attachment stage, are also electrically conducting.

[0005] The conductive areas of the circuit pattern, pads and through-holes may be formed from any conductive material or mixtures of different conductive materials. They are generally however, formed from copper. Since over time copper tends to oxidise to form a copper oxide layer with poor solderability, prior to passing to the second, component-attachment stage, a protective layer is coated over the pads and/or through-hole areas where it is desired to retain solderability to prevent formation of a poorly solderable surface layer of copper oxide.

[0006] While there is more than one way for preparing the bare boards, one of the most widely used processes for making the bare boards is known as the "solder mask over bare copper" (SMOBC) technique. Such a board generally comprises an epoxy-bonded fiberglass layer clad on one or both sides with conductive material. Generally, the board will be a multi-layer board having alternate conductive layers which comprise circuit pattern, and insulating layers. The conductive material is generally metal foil and most usually copper foil. In the SMOBC technique, such a board is obtained and holes are drilled into the board material using a template or automated drilling machine. The holes are then "plated through" using an electroless copper plating process which deposits a copper layer on the entirety of the board: both on the upper foil surfaces and on the through-hole surfaces.

[0007] The board material is then coated with a light sensitive film (photo-resist), exposed to light in preselected

areas and chemically developed to remove the unexposed areas revealing the conductive areas which are the plated through-holes and pads. Generally, in the next step, the thickness of the metal foil in the exposed areas is built up by a further copper electroplating step. A protective layer of an etch resist, which is usually a tin lead alloy electroplate composition is applied over the exposed and thickened copper areas.

[0008] The photo-resist is then removed exposing the copper for removal and the exposed copper surface is etched away using a copper etching composition to leave the copper in the circuit pattern finally required. In the next step, the tin-lead alloy resist is stripped away.

[0009] Since components will not be attached to the copper circuit traces, it is generally only necessary to coat the solder for attaching the components over the through-hole and pad areas but not the traces. Solder mask is therefore applied to the board to protect the areas where the solder coating is not required, for example using a screen printing process or photo-imaging technique followed by development and, optionally curing. The exposed copper at the holes and pads is then cleaned and prepared for solder coating and the protective solder coating subsequently applied, for example by immersion in a solder bath, followed by hot air leveling (HAL) to form a protective solder coating on the areas of copper not coated with solder mask. The solder does not wet the solder mask so that no coating is formed on top of the solder mask protected areas.

[0010] At this stage, the board comprises at least one insulating layer and at least one conductive layer. The conductive layer or layers comprise a circuit trace. The board also comprises a pad or pads and/or through-hole(s) protected from tarnishing by a layer of solder. A single conductive layer may comprise either a circuit trace or pad(s), or both. Any pads will be part of a conductive layer which is an outerlayer of a multi-layer board. The circuit traces on the board are coated with solder mask.

[0011] Such a board is ready to proceed to the second stage for attachment of the components. In this second stage, generally attachment of the components is achieved using solder: firstly a layer of solder paste (comprising solder and flux) is applied onto the boards, generally by printing and the components are positioned on the printed boards. The board is then heated in an oven to produce fusion of the solder in the solder paste, which forms a contact between the components and the board. This process is known as reflow soldering. Alternatively a wave soldering process is used in which the board is passed over a bath of molten solder. In either case additional solder is used over and above any protective solder coating.

[0012] The additional complications of attaching both legged components and the surface mount devices and the special requirements for mounting many small closely spaced components have resulted in increased demands on the surface protection coating for the conductive metal to which the components will be attached on the PCB's. It is essential that the finish applied by the bare board manufacturer does not leave a pad with an uneven surface as this increases the risk of electrical failure. It is also essential that the protective coating does not interfere with the subsequent solder step, thereby preventing formation of a good, con-

ducting bond between the bare board and components. An extra step in which the protective coating is removed would be undesirable.

[0013] As explained above, the conductive metal surfaces are generally formed of copper and the protective surface must be applied at the end of the first stage to prevent the formation of non-solderable copper oxide on the copper surfaces prior to the component attachment. This is particularly important because, generally speaking, the first stage and the second, component-attachment stage will be carried out at completely different sites. There may therefore be a considerable time delay between Formation of conducting pads and/or through-holes and the component-attachment stage, during which time oxidation may occur. Therefore, a protective coating is required which will retain the solderability of conducting material and enable a soldered joint to be made when the components are attached to the bare boards.

[0014] The most common protection coating presently used is tin/lead solder, generally applied using the "HAL" (hot air leveling) process, an example of which is described in detail above.

[0015] HAL processes are limited because it is difficult to apply the solder evenly and the thickness distribution produced by the use of HAL processes makes it difficult to reliably attach the very small and closely spaced components now being used.

[0016] Several replacement treatments for the HAL coating of a solder layer are being introduced. The coatings must enable formation of a reliable electrical contact with the component. They should also be able to stand up to multiple soldering steps. For example, as described above, there are now both legged and surface mount components for attachment to the bare boards and these will generally be attached in at least two soldering operations. Therefore, the protective coatings must also be able to withstand at least two soldering operations, so that the areas to be soldered in a second operation remain protected during the first operation.

[0017] Alternatives to the tin/lead alloy solder used in the HAL process, which have been proposed include organic protection, immersion tin or tin/lead plating and nickel/gold plating. In the nickel/gold process electroless plating of the copper surfaces is carried out in which a primer layer of nickel is applied onto the copper followed by a layer of gold. This process is inconvenient because there are many process steps and in addition, the use of gold results in an expensive process.

[0018] Organic protection for the copper pads during storage and assembly prior to soldering have also been effected using flux lacquer. Its use is generally confined to single-sided boards (i.e. boards which have conductive pads on only one side). The coating is generally applied by dip, spray or roller coating. Unfortunately, it is difficult to provide a consistent coating to the board surfaces so limited life expectancy, due to the porosity of the coating and to its inconsistent coating thickness, results. Flux lacquers have also been found to have a relatively short shelf life. A further problem is that in the component-attachment stage, if reflow soldering is to be used to attach the components, the components are held in place on the underside of the boards with adhesive. In cases where the flux lacquer is thick, the

adhesive does not bond the component directly to the printed board, but instead forms a bond between the adhesive and the lacquer coating. The strength of this bond can drop during the fluxing and soldering step causing components to be lost during contact with the solder baths.

[0019] One other alternative currently being used is passivation/protection treatment based upon the use of imidazoles or triazoles in which copper-complex compounds are formed on the copper surface. Thus, these coatings chemically bond to the surface and prevent the reaction between copper and oxygen. However this process is disadvantageous because it tends to be inadequate for withstanding successive soldering steps so that the high temperatures reached in a first soldering step tend to destroy the layer which cannot withstand a subsequent soldering operation needed to mount further components. One example of such a process is given in EP-A-0428383, where a process is described for the surface treatment of copper or copper alloys comprising immersing the surface of copper or copper alloy in an aqueous solution containing a benzimidazole compound having an alkyl group of at least 3 carbon atoms at the 2-position, and an organic acid.

[0020] Processes are also known which provide coatings using compositions which comprise silver.

[0021] The three common complexing systems for electroless silver plating processes are either ammonia-based, thiosulphate-based or cyanide-based

[0022] The ammonia systems are disadvantageous because the ammonia-containing silver solutions are unstable and explosive azides may tend to form. Thiosulphate systems are disadvantageous for use in the electronics industry because sulphur compounds in the silver coatings formed result in poor solderability so that in the subsequent component-attachment step, a poor electrical contact may be formed between the bare board and the component.

[0023] The cyanide-based systems are disadvantageous due to the toxicity of the plating solutions.

[0024] In U.S. Pat. No. 5,318,621 an electroless plating solution containing amino acids as rate enhancers for depositing silver or gold onto a nickel coating overlying copper on a circuit board is disclosed. It is described that neither gold nor silver electroless plating baths based on thiosulphate/sulphate will plate directly onto copper because the copper rapidly dissolves without allowing a silver or gold coating to form. In the introduction of the reference, "Metal Finishing Guidebook & Directory" (1993 edition), silver plating solutions comprising silver nitrate, ammonia and a reducing agent such as formaldehyde are mentioned.

[0025] U.S. Patent No. 4,863,766 also discloses electroless silver plating, using a cyanide-based plating solution. In Metal Finishing (1983) 81(i), pp 27-30 Russev described immersion silvering of copper powder from a plating solution containing silver nitrate and a nitrogen complexing agent. In Metal Finishing (1960) August, p 53 Geld described a silver coating process involving an initial bright dip of the brass or copper substrate, followed by a silver plating step in which a thick coating of silver is plated from a solution of silver nitrate and potassium iodide. The process is for plating of electrical contacts to increase conductivity.

[0026] In JP-A-04-110474 a base material is plated with silver, dried and subsequently treated with a mercaptan compound to prevent tarnish.

[0027] In DE-C-4316679 base metals such as copper are coated with palladium in a two-step process including a first step in which the surface is contacted with a bath containing a palladium salt and an oxidizing agent, and in the second step with a bath containing a palladium salt, a completing agent and formic acid or formic acid derivative. The latter bath may also contain stabilizers for the bath itself, which stabilize the bath against decomposition or "plating-out". It is suggested that the copper substrate should previously be etched using a non-bright etch bath including persulphate. However, such pretreatment steps tend to produce relatively porous coatings. The inventors there minimize the porosity of the coating by using the two-step process in the first of which a very thin coating is formed. This reference warns against using silver as corrosion protection due to migration.

[0028] The present invention relates to a displacement immersion metal plating in which a more electropositive metal displaces a less electropositive metal at the surface to be coated. Ions of the more electropositive metal oxidize the substrate metal. A displacement plating process differs from an electroless process because the silver coating forms on the surface of a metal by a simple displacement reaction due to the relative electrode potentials of the oxidisable metal of the surface to be protected and of the silver ions respectively.

[0029] It is reported in for example "Modern Electroplating" by F. A. Lowenheim, published by J. Wiley & Sons (1963) that silver will plate by displacement on most base metals but that immersion plated silver is poorly adherent. F. A. Lowenheim there suggests that when electroplating base metals with silver, it is necessary to deposit first a thin film of silver on the work piece from a high-cyanide strike bath to ensure good adhesion of the subsequent electroplated silver layer.

SUMMARY OF THE INVENTION

[0030] The present invention aims to provide an alternative to the solder protection coating for the copper or other conducting surfaces of bare boards which require protection from tarnishing between bare board manufacture and the component-attachment stage.

[0031] In accordance with the present invention, there is provided a method for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the process comprising contacting the pads and/or through-holes with a bright-etch composition in a bright-etch step; and subsequently immersion plating the etched pads and/or through-holes in a metal-plating step to form solderable plated metal surfaces.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032] **FIG. 1** is a graphical representation illustrating an example described in the present application.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0033] The insulating layer and conducting layer of the PCB will be as described immediately above. They may comprise the insulating layer and conducting circuit pattern of any conventional PCB, respectively. The pads and/or

through-holes for plating are those areas of the PCB for which solderability must be maintained for attachment of components in the subsequent soldering steps for component attachment.

[0034] The bright-etch step comprises contacting the pads and/or through-holes with a bright-etch composition. Such compositions are already known in the industry for other applications and they produce a bright smooth cleaned surface on the conducting metal from which the pads and/or through-holes are formed. In contrast, non-bright etch compositions, such as those which are based on persulphate provide microroughened, cleaned surfaces. The use of the bright-etch step allows the formation of a dense, nonporous metal coating, which is particularly suitable for a subsequent soldering step.

[0035] Suitable bright-etch compositions are generally aqueous and may be based for example on one or mixtures of more than one of hydrogen peroxide, sulphuric acid, nitric acid, phosphoric acid or hydrochloric acid. The bright-etch compositions generally include at least one component which will tend to modify the dissolution of copper in bright-etch compositions.

[0036] Particularly preferred bright-etch compositions where the metal surface of the pads and/or through-holes comprises copper or a copper alloy are, for example, as described in JP 62-188785 A2 (comprising 5.1-10.2 moles/l nitric acid, 4.6-9.2 moles/l sulphuric acid, 0.01 moles/l zinc nitrate and 0.4 moles/l copper nitrate in aqueous solution); JP 60-190582 (comprising for example 20-50% by weight sulphuric acid (96%), 10-25% by weight nitric acid (67.5%), 0.5-1a by weight hydrochloric acid (35%) and 0.5-1% by weight nonionic surfactant); U.S. Pat. No. 3,668,131 (comprising hydrogen peroxide, sulphuric acid and urea additives); Metal Finishing (February 1986), 84, (2), 67-70 (comprising sodium dichromate, sulphuric acid, hydrochloric acid, sodium diethyldithio carbonate); Trans Inst. Metal Finishing (Summer 1983), 61, (2), 46-49 (acidified hydrogen peroxide comprising hydrogen peroxide, sulphuric acid and stabilizer); Oberfläche Surf, (Aug 1979) 20, (8), 178-179 (comprising nitric acid and dodecyl pyridinium chloride); U.S. Pat. No. 4,510,018 (comprising sulphuric acid, hydrogen peroxide, fatty acid amine and ammonium compound); U.S. Pat. Nos. 4,459,216 (comprising 5-100 g/l hydrogen peroxide and 100-300 g/l sulphuric acid and aromatic stabilizer); JP 84-038,308 (comprising 0.15-0.3 moles/l hydrochloric acid; 0.2-0.4 moles/l phosphoric acid and 0.02-0.1 moles/l sulphuric acid). Where the conducting material of the pads and/or through-holes comprises stainless steel, particularly preferred bright-etch compositions may be as described for example in WO 93-08317; JP 62-238,379 A2; DE 1,928,307; or Tr. Gos. Nauchno-Issled Proektn. Inst. Osnovn. Khim (1974), 36, 93-97. Where the conducting material is aluminium, a suitable bright-etch is as described in Met. Finishing (July 1986) 84, (7), 55-59.

[0037] Thus, any etch composition which provides a bright, cleaned surface may be used. In the bright-etch step, contact with the bright-etch composition may be by immersion, spray or any other coating technique, such as is described in any of the references above, for sufficient time and at a suitable temperature to enable a bright surface to form on the conducting material of the pads and/or through-holes. Generally the temperature for contact with the bright-

etch composition will be ambient and the contact time will be from 5 seconds to 10 minutes, preferably at least 30 seconds, or even at least 2 minutes, and preferably for no greater than 5 minutes.

[0038] Generally after the etching step, there will be a post-rinse step comprising rinsing with deionized water and generally without drying, the bare boards then proceed directly to the plating step. Alternatively, an acid rinse step may be included, after the aqueous rinse.

[0039] The plating step is an immersion (or displacement) plating step. In an immersion plating step, the plating composition comprises metal ions of a metal which is more electropositive than the conducting material. The choice of metal ions in the immersion plating solution, therefore depends on the metal to be plated. Since the pads or through-holes generally comprise copper or nickel, suitable examples of plating metals include bismuth, tin, palladium, silver and gold; silver and bismuth ions are particularly preferred.

[0040] A particularly preferred immersion silver plating method is described in our copending British application filed on even date herewith under the application number 9425030.5, and subsequent U.S. Ser. No. _____ (attorney docket no A0626/7001).

[0041] As sources of plating metal ions, any water soluble metal salt may be used, for example nitrates, acetates, sulphates, lactates or formates. Preferably silver nitrate is used.

[0042] The metal plating ions are generally in the plating composition at a concentration of from 0.06 to 32 g/l (based on metal ions), preferably from 0.1 to 25 g/l, most preferably from 0.5 to 15 g/l.

[0043] Contact of the metal surface with the plating solution will generally be at temperatures of from 10 to 90° C., preferably 15 to 75° C., more preferably 20 to 60° C. For example, the temperature of contact with the plating solution will be from 15 to 50° C., most usually from 20 to 40° C.

[0044] Contact can be by any method, usually dip, spray or horizontal immersion coating. Spray coating is preferred. Such contact may be part of a substantially continuous coating process.

[0045] The contact time of the plating solution with the metal surface is sufficient to form plated metal surfaces over the metal. Generally the contact time will be from 10 seconds to 10 minutes. A contact time of less than 10 seconds has generally been found to give insufficient coverage with silver coating and although the contact time may be longer than 10 minutes, no additional benefit has been found from a contact time of longer than 10 minutes.

[0046] The preferred plating process is an immersion displacement process and not a true electroless plating process. In the preferred plating compositions of the present invention, metal atoms on the surface of the metal are oxidized by the metal plating ions in the solution, so that a layer of plated metal deposits on the pads and/or through-holes. The process is self-limiting because when plated metal covers all of the surface sites of metal oxidizable by the plating metal no further reaction and therefore no further deposition occurs.

[0047] In a second aspect of the invention, there is provided for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising metal plating the etched pads and/or through-holes by contact with a plating composition in a metal plating step to form solderable plated metal surfaces and contacting the plated metal surfaces with a solution of a tarnish inhibitor.

[0048] In this aspect of the invention, preferably, prior to contacting the metal surface with the plating composition in the plating step, the metal surface is cleaned. Cleaning may be using an acidic cleaning composition, such as any cleaning composition known in the art. Examples are copper conditioner PC 1144 supplied by Alpha Metals Limited of the United Kingdom. Where there is a cleaning step using an acidic cleaning solution, generally there will be a rinsing step prior to contacting the metal surface with the plating solution. Preferably any pre-cleaning will include a bright-etch step. In both aspects of the invention, the tarnish inhibitor may be present in the plating solution itself so that the plating solution comprises the solution comprising tarnish inhibitor. Thus, in a preferred method of the invention, the plated metal surfaces are contacted with a solution comprising a tarnish inhibitor during the plating step (i.e., contact may be during formation of the plated metal surfaces).

[0049] Alternatively, the metal surfaces are formed in the plating step and subsequently the formed metal surfaces are contacted with a solution comprising a tarnish inhibitor in a further step. The solution is preferably aqueous, being made up from deionized or otherwise purified water. The composition comprising tarnish inhibitor may additionally comprise solubilizers, for example non-aqueous solvents, surfactants and/or pH buffers.

[0050] Contact of the composition comprising tarnish inhibitor with the plated metal surfaces will be for at least 5 seconds, preferably for at least 20 seconds. Where the tarnish inhibitor is present in the plating solution, the time of contact is generally determined by the duration of the plating step. Generally, the contact time will be from 1 to 5 minutes. The temperature of contact is most usually from 10 to 90° C., preferably 15 to 75° C., more preferably 20 to 60° C. For example the temperature of contact with the plating solution may be from 15 to 50° C., most usually from 20 to 40° C. Contact may be by any conventional means, for example by dip, spray or horizontal immersion coating.

[0051] The most appropriate pH depends to some extent on the particular tarnish inhibitor used but primarily on the metal ions present in a plating bath which contains the tarnish inhibitor. Where the tarnish inhibitor is contacted in a separate step with the plated metal surface, the pH should be appropriate for the tarnish inhibitor and selected so that it does not attack the plating. Where the solution is a silver plating composition, a convenient pH is in the range of 3 to 10. Where the solution is a bismuth plating composition, the pH may be 1 or lower.

[0052] The solution comprising the tarnish inhibitor may be a final rinse solution, applied to the boards prior to drying of the boards. The board may undergo subsequent treatment steps after contact with the composition comprising tarnish inhibitor. However, generally, after contact with the solu-

tion, comprising a tarnish inhibitor and drying, they are at the end of the first bare board manufacturing stage, and are ready for the second component-attachment stages. Optionally, for example, there may be a deionized water rinse step, prior to drying.

[0053] The concentration of tarnish inhibitor in the solution comprising tarnish inhibitor, will generally be from 0.0001 to 5% by weight, i.e. 0.001 to 50 g/l. Preferably, the amount of tarnish inhibitor will be from 0.005 to 3% by weight, and most preferably from 0.01 to 2% by weight, or even below 1% by weight.

[0054] The method of the second aspect of the invention may surprisingly also be used on precious metals such as gold, platinum or ruthenium where it will improve solderability.

[0055] In the second aspect of the invention, the metal plating step is preferably an immersion/displacement plating or electroless plating step. It consists of a single step using a single plating composition. Most preferably the plating step will be an immersion/displacement plating step comprising contacting the metal of the pads and/or through-holes with an immersion plating composition.

[0056] Where the plating is other than by the preferred immersion/displacement process, for example, if it is by electroless plating, the plating composition may comprise alternative plating metal ions, such as nickel.

[0057] The use of tarnish inhibitor in the invention has been found to provide metal coatings which have good tarnish resistance (resistance to humidity and oxidation) even when stored at 40° C. and 93% RH for 96 hours or at 150° C. for 2 hours. The porosity inherent in immersion coatings is reduced by the provision of a level surface using the bright-etch step and using, so that the anti-tarnish properties are considerably improved, even at the high temperatures reached in reflow soldering processes. Concern over the use of silver plating as described for example in DE-C-4316679 due to migration of silver ions is overcome as it has been found that the present invention substantially prevents silver migration by providing a barrier to moisture.

[0058] In both the above aspects of the invention, an immersion plating composition preferably contains a complexing agent for the ions of the more electropositive metal.

[0059] In a further aspect of the present invention there is provided a displacement metal plating process in which a relatively less electropositive base metal is plated with a relatively more electropositive coating metal by contact with an aqueous plating composition containing ions of the more electropositive metal, a completing agent for such ions and a tarnish inhibitor for the more electropositive metal so as to form a coating of the more electropositive metal.

[0060] In this aspect of the invention there is also provided is a new plating composition containing ions of a metal which can be displacement plated, a completing agent for the ions, preferably present in higher than equimolar amounts as compared to the metal ion, and containing a tarnish inhibitor for the said metal, and being substantially free of reducing agent capable of reducing the ions to the metal.

[0061] This aspect of the invention has been found to be particularly useful for silver or bismuth plating. Therefore preferably, the plating composition described contains silver or bismuth ions.

[0062] The plating composition used in this aspect of the invention may be a immersion plating composition based on any plating composition used in the PCB industry.

[0063] In this embodiment of the invention, preferably, prior to contacting the metal surface with the plating composition in the plating step, the metal surface is cleaned. Cleaning may be accomplished using an acidic cleaning composition, such as any cleaning composition known in the art. Examples are copper conditioner PC 1144 supplied by Alpha Metals Limited.

[0064] Where there is a cleaning step using an acidic cleaning solution, generally there will be a rinsing step prior to contacting the metal surface with the plating solution.

[0065] Preferably any pre-cleaning will include a bright-etch step.

[0066] The plating composition may also comprise a complexing agent. If so, the complexing agent is preferably present in an amount of from 0.1 to 250 g/l, preferably from 2 to 200 g/l and most preferably from 10 to 100 g/l, especially around 50 g/l. The complexing agent may be any complexing agent for the plating metal ions which does not form a water insoluble precipitate under the aqueous and pH conditions of the composition. Mixtures of complexing agents may also be used. It is desirable to use complexing agents which are bi-dentate or higher dentate ligands since the stability constants of such complexes are higher than mono-dentate ligands.

[0067] Examples of suitable complexing agents have oxygen-containing ligands, for instance amino acids and their salts, preferably having at least 2 and up to 10 carbon atoms, polycarboxylic acids, usually amino acetic acids, such as nitrilo-triacetic acid or, usually, alkylene polyamine poly-acetic acids including ethylene diamine tetra-acetic acid (EDTA), diethylene triamine penta-acetic acid, N-hydroxyethyl ethylene diamine triacetic acid, 1,3-diamino-2-propanol-N,N,N',N'-tetra-acetic acid, bishydroxyphenylethylene diamine diacetic acid, diamino cyclohexane tetra-acetic acid or ethylene glycol-bis-[(β -aminoethylether)-N,N'-tetra-acetic acid] and N,N,N',N'-tetrakis-(2-hydroxypropyl) ethylene diamine, citrates and/or tartrates, N,N-di-(hydroxyethyl) glycine, gluconates, lactates, citrates, tartrates, crown ethers and/or cryptands.

[0068] Particularly preferred complexing agents for silver are EDTA, DTPA and N,N,N',N'-tetrakis-(2-hydroxypropyl) ethylene diamine. The complexing agent should form a soluble complex with plating metal ions in aqueous solution under the pH conditions of the plating solution.

[0069] A suitable complexing agent for bismuth is chloride, and it is generally unnecessary to use a multidentate (i.e., bi- or higher dentate) ligand complexing agent for bismuth.

[0070] The complexing agent is preferably used either in stoichiometric equivalent amounts or in a stoichiometric excess so that all the plating metal ions may be complexed. By stoichiometric we mean equimolar. Preferably the complexing agent is present in a higher molar concentration than the silver ions, the molar ratio preferably being (at least 1.2):1, more preferably (at least 2.0):1, more preferably (at least 3):1.

[0071] Suitable tarnish inhibitors for use in all aspects of the present invention include for example:

[0072] (a) fatty acid amines, preferably having at least 6 carbon atoms, most preferably at least 10 carbon atoms and generally no greater than 30 carbon atoms, they may be primary, secondary, tertiary, diamines, amine salts, amides, ethoxylated amines, ethoxylated diamines, quaternary ammonium salts, quaternary diammonium salts, ethoxylated quaternary ammonium salts, ethoxylated amides and amine oxides. Examples of the primary, secondary and tertiary amine-type corrosion inhibitors are ARMEEN™ to (™ denotes trademark). Examples of the subsequent amine-type corrosion inhibitors are respectively DUOMEEN™, ARMAC™/DUOMAC, ARMID™, ETHOMEEN™, ETHODUONEEN™, ARQUAD™, DUOQUAD™, ETHOQUAD™, ETHOMID™, AROMOX™, all supplied by Akzo Chemie.

[0073] (b) purines and substituted purines.

[0074] (c) N-acyl derivatives of sarcosine, such as the SARKOSYrange of products supplied by Ciba-Geigy.

[0075] (d) organic polycarboxylic acids such as Reo-cor 190 supplied by Ciba-Geigy.

[0076] (e) substituted imidazoline in which substituents are for example hydroxyl Cl_{1-4} alkyl amino or carbonyl-containing groups. Examples include AMINE 0, produced by Ciba-Geigy, especially in combination with a N-acyl sarcosine of category (c).

[0077] (f) alkyl or alkyl benzyl imidazoles, e.g. undecyl imidazole in which the alkyl group has up to 22 carbon atoms, preferably no greater than 11 carbon atoms and in which the alkyl or benzyl groups are optionally substituted.

[0078] (g) benzimidazoles, especially alkylaryl benzimidazoles in which the alkyl group has up to 22 carbon atoms, preferably no greater than 10 carbon atoms and in which the alkyl or benzyl groups are optionally substituted, for example 2-(p-chlorobenzyl) benzimidazole which is particularly preferred.

[0079] (h) phosphate esters such as EKCOL PS-413, supplied by Witco.

[0080] (i) optionally substituted triazole derivatives such as REOMET 42, supplied by Ciba-Geigy. Examples are benzo triazole, tolyl triazole and alkyl substituted triazole derivatives having a carbon number on the alkyl group of from 1 to 22, preferably from 1 to 10.

[0081] (j) substituted tetrazoles, such as 5(3(trifluoromethyl phenyl)) tetrazole, is also a preferred example.

[0082] The choice of tarnish inhibitor will depend to some extent upon the metal of the plated metal surfaces, but this will be clear to a person skilled in the art. For example, if the tarnish inhibitor is to be incorporated into a gold plating bath, the tarnish inhibitor may be a chloride salt, however,

in contrast, using a silver plating bath, chloride salts may not be used as they will result in formation of an insoluble silver chloride precipitate.

[0083] The tarnish inhibitor is preferably water soluble so that the solution is an aqueous solution. However, water immiscible tarnish inhibitors may be used although it may be necessary to include a surfactant/cosolvent in the solution.

[0084] This invention has been found to provide considerable advantages in preventing tarnishing and conferring humidity resistance on the bare boards produced to that additional protection is provided between the bare board manufacture stage and the component-attachment stage. Solderability is found to be enhanced.

[0085] A suitable pH for a silver plating composition may be from 2 to 12, but is preferably from 4 to 10. Thus, the composition may be acidic, up to pH 7. Alternatively, the composition may be alkaline, and have a pH of greater than 7, or even greater than 7.5. A bismuth plating solution usually has a low pH of 1 or less.

[0086] A buffering agent may be included in the plating composition to ensure that the pH of the composition is within the desired range. As the buffering agent, any compatible acid or base may be included. A compatible acid or base is an acid or base which in the amounts required in the composition does not result in the precipitation out of solution of the silver ions and/or complexing agent. For example hydrogen chloride is unsuitable for a silver plating composition as it forms an insoluble silver chloride precipitate. Suitable examples include sodium or potassium hydroxide or a carbonate salt, or where acids are required, suitable acids may include citric acid, nitric acid or acetic acid. Borates, phthalates, acetates, phosphonates may be used but the buffer should not result in precipitation of the metal salts and preferably does not inhibit the plating rate. An appropriate buffer will be dependent on the desired working pH.

[0087] The plating composition may include optional ingredients such as surfactants or wetting agents to improve the coating uniformity. Where surfactants are included, preferably they are introduced into the composition in an amount such that in the plating bath, they will be present at a concentration of from 0.02 to 100 g/l. Preferably they will be incorporated at a concentration of from 0.1 to 25 g/l and most preferably at a concentration of from 1 to 15 g/l. Any standard surfactant or wetting agent useful in a plating bath may be used. Nonionic surfactants are preferred. Particularly preferred surfactants are alkyl phenol ethoxylates, alcohol ethoxylates and phenol ethoxylates such as *Synperonic NP9 (ex. ICI), *Synoeronic A14 (ex. ICI) and *Ethylan HB4 (ex. Harcros), respectively (*denotes trade name).

[0088] A further optional ingredient which can be included in the plating baths of the present invention are grain refiners. Grain refiners improve the appearance of the plated metal surfaces by causing formation of smaller crystals of plated metal having a more densely packed structure. Suitable examples of grain refiners include lower alcohols such as those having from 1 to 6 carbon atoms, for example isopropanol and polyethylene glycols, for example PEG 1450 (Carbowax* Union Carbide). Grain refiners may be incorporated in the composition in amounts from 0.02 to 200

g/l. More preferably, if a grain refiner is included, it will be at concentrations of from 0.05 to 100 g/l and most preferably from 0.1 to 10 g/l. Any nonaqueous solvent should be present in amounts below 50% by weight of the composition, preferably below 30% by weight or even below 10% or 5% by weight of the plating composition.

[0089] Other non-active, non-interfering components may be included such as defoamers especially for spray applications (e-g., A100 supplied by Dow), dyes, etc.

[0090] The balance in the composition is water. Deionized water or other purified water which has had interfering ions removed, is used in the plating composition used in the process of the invention.

[0091] In order to form the plating composition for use in the processes of the present invention, preferably a solution is firstly prepared comprising deionized water, complexing agent as defined above, and any buffering agent, optionally with the other optional ingredients, and a salt of the more electropositive metal is added as an aqueous solution to the other components which have been formed into a pre-mix. It has been found that this is the most advantageous way to prepare the solution because trying to dissolve the metal salt directly into the plating composition is relatively time consuming and, where the metal is silver, tends to be more vulnerable to photo-reaction which results in precipitation of silver ions out of solution, as a dark precipitate.

[0092] Preferably the pH of the composition to which a silver salt is added will be from pH 3 to 10, most preferably from 4 to 8.

[0093] The components are mixed until they have substantially dissolved. The use of heat for silver dissolution is disadvantageous because again, it may tend to cause the formation of a dark silver precipitate.

[0094] After contact of the bare board with the solution comprising tarnish inhibitor, the board is dried. Preferably, there will be no post-rinse step between contact of the board with the solution and drying.

[0095] Drying may be by any means, but is generally using warm air, for example treated metal may be passed through a drying oven

[0096] The coating obtained using the method of the present invention produces a surface which is considerably more uniform and even than that obtained in the conventional HAL processes and, compared with organic protection, the coating is more resistant to soldering operations. Furthermore, the process of this invention is less expensive and simpler than use of the nickel/gold process.

[0097] In the subsequent component-attachment stage, the components are soldered onto the plated pads and/or through-holes of the bare board. The metal of the pad(s) and/or through-holes (generally copper) and plating metal, usually silver, and/or the plating metal and solder may tend to intermix. The bond formed with the components has good electrical conductivity and good bond strength.

[0098] After component attachment, finished boards having components attached over the plated layer of the present invention, do not suffer joint reliability problems as do those boards formed using a nickel/gold step.

EXAMPLE 1

[0099] A composition was prepared in which 50 g EDTA and 20.4 g of solid sodium hydroxide were mixed with sufficient water to dissolve them. A solution comprising 1 g silver nitrate in deionized water was subsequently added to the premixture comprising EDTA and sodium hydroxide solution and deionized water was added to 1 litre. Copper double-sided circuit boards, having a variety of surface mount feature and plated through-holes of various diameter were coated with the silver solution using the following procedure.

[0100] Boards were chemically brightened in an aqueous solution of 20% v/v H_2O_2 (35%), 0.5% v/v H_2SO_4 , (96%), 2.5% 1,4-butanediol for 1 minute. A tap water rinse was then employed, followed by an acid rinse in 10% H_2SO_4 , for 1 minute. The boards were given a further water rinse, then immersed in the silver plating solution at 40° C. for 4 minutes. After removal from the bath, the boards were rinsed with water and warm air dried. Copper areas of the board were coated with a bright, even silver deposit.

[0101] Coated boards were subjected to three passes through a typical IR silver paste reflow profile (see FIG. 1), then wave soldered using NR300, an Alpha Metals VOC free, no clean flux. 100% filling of the plated through-holes with solder was achieved.

[0102] Further boards were stored in a humidity cabinet at 40° C./93% RH for 24 hours before being passed through 3 IR reflow profiles. These boards showed a slight degree of tarnishing on the silver coating. However 100% hole filling was still achieved during subsequent wave soldering with NR 300 flux.

EXAMPLE 2

[0103] A silver plating solution was prepared by forming a solution comprising 50 g EDTA, 20.4 g NaOH, 14 g Ethylan HB4 (Akros Chemicals), 3 g Crodamet 02 (Croda Chemicals) in 800 mls deionized water. To this solution was added a solution of 1 g $AgNO_3$ in 100 mls deionized water. The pH was adjusted to 6.8 by addition of dilute NaOH/ HNO_3 , then made up to 1 litre with deionized water.

[0104] Double sided bare copper boards were coated with the above solution using the procedure as described in Example 1. 100% filling of plated through-holes with solder was achieved during wave soldering with NR300 flux after passage through 3 IR reflow profiles.

[0105] Boards stored at 40° C./93% RH for 24 hours prior to passage through 3 IR reflow profiles showed no evidence of tarnishing and soldered well during wave soldering trials, giving 100% hole filling.

EXAMPLE 3

[0106] Double-sided bare copper boards were coated using the bath composition and procedure as described in Example 1. Following removal of the boards from the silver plating solution and rinsing, the boards were immersed in a solution of 4 g Reomet 42 (Ciba-Geigy) in 1 litre deionized water (pH 7) for 1 minute at room temperature. The boards were then rinsed in tap water and warm air dried. A bright even silver coating was produced.

[0107] The coated boards were stored at 40° C./93% RH for 24 hours then passed through 3 IR paste reflow profiles. The boards showed no evidence of tarnishing, and soldered well when wave soldered using KR 300 flux.

EXAMPLE 4

[0108] Coupons of copper strip (5 cm×1 cm) were coated with the silver coating as described in Example 2. In addition, further samples were coated with immersion tin, 63/37 Sn/Pb and two competitors solderability preservative coatings based on substituted benzimidazole chemistry. The following coating procedures were applied for the various samples:

[0109] Immersion Tin Coating

[0110] Coupons were etched in an aqueous solution of Na₂S₂O₈ (5%), H₂SO₄ (5%) for 2 minutes, rinsed with tap water, then rinsed with 10% H₂SO₄ for 1 minute and then rinsed with deionized water. The coupons were then immersed in an immersion tin plating solution comprising 0.33 g/l Sn(BF₄)₂, 150 g/l thiourea, 20 g/l fluoroboric acid and 5 g/l Synparonic NP9 (ex. ICI) in deionized water, for 1 minute at room temperature. The coupons were then rinsed with deionized water and warm air dried.

[0111] Sn/Pb Coating

[0112] Coupons were etched in an aqueous solution comprising Na₂S₂O₈ (5%) and H₂SO₄ (5%), rinsed with tap water then with 10% H₂SO₄ and then with deionized water. The coupons were warm air dried. Alpha NR 300 flux was then applied to each coupon. The coupons were then coated 63/37 Sn/Pb by immersion in molten solder at 250° C. for 3 seconds.

[0113] Azole 1 and Azole 2

[0114] Coupons were etched and rinsed as for the immersion tin samples. Coupons were then immersed in the solution containing the azole at 40° C. for 90 seconds. After removal from the azole containing solution, the coupons were rinsed with deionized water, and warm air dried.

[0115] The coupons were subjected to a variety of different pretreatments.

A.	No pre-treatment.
B.	Passage through 3 solder paste reflow profiles.
C.	Storage at 40° C./93% RH for 96 hours.
D.	Storage at 40° C./94% RH for 96 hours, then 3 solder paste reflow profiles.
E.	Storage at 150° C. for 2 hours.

[0116] Samples were then soldered using a meniscograph with NR300 flux.

[0117] The meniscograph test method monitors the solderability by measuring the net force acting between specimen and solder. The coatings are assessed by the length of time to reach zero wetting force, and the size of the equilibrium wetting force. To achieve good results in wave soldering a short wetting time and high equilibrium wetting force are preferred.

[0118] The table below shows the wetting times in seconds and wetting forces after 2 seconds immersion in mN/mm for various copper coated samples.

[0119] As can be seen from above, the silver coatings prepared according to this invention have shorter wetting times and higher wetting forces than the Sn and benzimidazole alternative and retain these properties more readily after humidity and heat treatment.

TABLE 1

Coating	Pre-Treatment	Wet Time/Sec	Wetting Force at 2 Seconds
Example 2	A	0.7	0.429
Example 2	B	0.8	0.444
Example 2	C	0.7	0.429
Example 2	D	0.7	0.441
Example 2	E	0.8	0.438
Tin	A	0.9	0.488
Tin	B	>5	-0.028
Tin	C	>5	0.008
Tin	D	>5	-0.148
Azole 1	A	0.8	0.439
Azole 1	B	0.9	0.412
Azole 1	C	0.9	0.443
Azole 1	D	0.9	0.426
Azole 1	E	1.0	0.421
Azole 2	A	0.9	0.449
Azole 2	B	1.0	0.417
Azole 2	C	0.9	0.466
Azole 2	D	1.1	0.310
Azole 2	E	1.2	0.296
Sn/Pb	A	0.8	0.475
Sn/Pb	B	0.8	0.501
Sn/Pb	C	0.8	0.492
Sn/Pb	D	0.8	0.474
Sn/Pb	E	0.8	0.492

EXAMPLE 5

[0120] A displacement bismuth plating composition was prepared comprising 3.9 g bismuth oxide, 183.1 g hydrogen chloride (as 37% solution), 490. Sg glycolic acid (70% solution), 265.4 g (50% sodium hydroxide solution), 0.077 g potassium iodide, 0.003 g Synperonic NP9 (ex. ICI) and 4 g 2p-chlorobenzyl benzimidazole, were added to deionized water to make 1 liter of product solution. Bare boards having copper pads and copper through-holes were chemically brightened as described in Example 1, then immersed in the plating baths for 2 minutes at 70° C. A coating of bismuth was formed on the surface of the copper having a thickness of 0.054 μm. Subsequent solderability and tarnish resistance tests carried out on the plated bare boards showed good results for solderability and tarnish resistance.

EXAMPLE 6

[0121] Double-sided bare copper boards were bright etched in an aqueous solution of 50% v/v HNO₃, 10% H₂SO₄, 10% H₃PO₄, 1% HCl for 1 minute at room temperature. Boards were then rinsed in tap water followed by 10% H₂SO₄ for 1 minute. After a further water rinse, boards were immersed in silver plating bath described in Example 2 for 4 minutes at 45° C. Boards were then water rinsed and warm air dried.

[0122] The coated boards were stored at 40° C./93% RH for 24 hours then passed through 3 IR paste reflow profiles. The boards showed no evidence of tarnishing when wave soldered using NR 300 flux.

EXAMPLE 7

[0123] A silver plating bath was prepared by forming a solution comprising 64.8 g diethylene triamine penta-acetic

acid, 23.0 g NaOH, 24 g surfactant Ethylan HB4 (Akros Chemicals), 2.5 g Crodamet 02 an ethoxylated 3° amine compound (Croda Chemicals) in 800 mls deionized water. To this solution was added a solution of 1 g silver nitrate in 100 mls deionized water. The pH of this solution was adjusted to 6.9 by addition of dilute NaOH solution or nitric acid. The volume was then made up to 1 litre using deionized water.

[0124] Double-sided bare copper boards were coated using the above solution using the procedure as described in Example 1. 100% filling of the plated through-holes was achieved during wave-soldering of the coated boards using Alpha Metals MR300 flux after passage through 3 IR reflow profiles showed no evidence of tarnishing, and soldered well during wave-soldering trials giving 100% hole-fill.

EXAMPLE 8

[0125] An immersion silver plating solution was prepared comprising 98.2 g deionized water, 1 g of nitric acid, 0.1 g of silver nitrate, 0.3 g of Chemeen C2 (antitarnish) and 0.4 g Mazawet DF (solubilizer). The pH was adjusted to 6 using a 50% solution of ethylene diamine. The bath produced an adherent silver deposit on copper coupons which showed good solderability and humidity resistance.

EXAMPLE 9

[0126] A bismuth plating solution was prepared containing bismuth trioxide 2.1% weight, hydrochloric acid (22° Be) 46.73% weight, glycollic acid (70%) 49.5% weight, potassium chloride 0.07% weight, polyethylene glycol 600 0.1% weight, Chemax Chemeen C2 0.2% weight, distilled water 1.2% weight and tartaric acid 0.1% weight. A further solution was prepared from which the Chemeen C2 was omitted. Samples of copper clad printed circuit material were plated in each of the solutions. These plated samples were then placed in a humidity chamber for 16 hours at 60° C. and 95% relative humidity.

[0127] After this exposure the samples were examined, and those prepared in the solution without the Chemeen C2 were heavily tarnished. The samples prepared in the solution containing the tarnish inhibitor had a good appearance with minimal oxidation, and when tested showed good solderability.

[0128] Other embodiments of the invention are to be considered within the scope of the appended claims.

What is claimed is:

1. A method for coating a printed circuit board comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising contacting the pads and/or through-holes with a bright-etch composition in a bright-etch step; and subsequently metal plating the etched pads and/or through-holes by contact with a plating composition comprising ions of a metal which is more electropositive than the metal from which the pads and/or through-holes are formed and being substantially free of reducing agent for said ions in an immersion metal plating step to form solderable plated metal surfaces.

2. A method according to claim 1 in which the plated metal surfaces are contacted with a solution of a tarnish inhibitor.

3. A method for coating a printed circuit board comprising an insulating layer and a conducting layer, with metal pads

and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising metal plating the etched pads and/or through-holes by contact with a plating composition in a metal plating step to form solderable plated metal surfaces and contacting the plated metal surfaces with a solution of tarnish inhibitor.

4. A method according to claim 1 in which the metal plating step is a method in which a metal which is more electropositive than the metal of the said pads and/or through-holes is immersion/displacement coated from an aqueous solution containing ions of the more electropositive metal substantially free of reducing agent for said ions.

5. A method according to claim 1 in which the plating composition contains a complexing agent for the said ions, preferably a multidentate ligand complexing agent.

6. A method according to claim 1 or claim 3 in which the plating composition comprises a tarnish inhibitor and in the process, the metal surfaces are contacted with a solution comprising a tarnish inhibitor during the plating step, so that the tarnish inhibitor is present in the metal plating composition.

7. A method according to claim 1 or claim 3 in which the metal plated surfaces are formed in the plating step and subsequently the pre-formed plated metal surfaces are contacted with a solution comprising a tarnish inhibitor in a posttrise second step.

8. A method according to claim 2 or claim 3 in which the contact time of the plated metal surfaces with the solution comprising a tarnish inhibitor is from 10 seconds to 5 minutes.

9. A method according to claim 2 or claim 3 in which the metal surfaces are contacted with a solution comprising a tarnish inhibitor by dip coating or spray coating.

10. A method according to claim 2 or claim 3 in which the tarnish inhibitor is present in the solution in an amount of from 0.001 to 5% by weight of the solution.

11. A method according to claim 1 in which the metal coating of the plated metal surfaces comprise nickel, silver, tin, lead, palladium, cobalt, gold, platinum or bismuth or their alloys, preferably silver.

12. A method according to claim 1 in which the pads or through-holes are formed of copper.

13. A method according to claim 1 including a preliminary step of applying to exposed conductor traces at the surface of the PCB a mask which is an insulator, such that the pads and/or through-holes are left exposed.

14. A method according to claim 1 including a subsequent step of attaching conducting components to the metal plated pads and/or through-holes using solder in direct contact with the metal plating.

15. An aqueous plating composition suitable for forming an immersion plating of a relatively more electropositive metal on a relatively less electropositive metal substrate containing ions of the more electropositive metal and a complexing agent for the ions and a tarnish inhibitor for the more electropositive metal and being substantially free of reducing agent for said ions.

16. A composition according to claim 15 in which the tarnish inhibitor is present in the solution in an amount of from 0.001 to 5% by weight of the composition.

17. A composition according to claim 15 in which the said ions are of nickel, silver, tin, lead, palladium, cobalt, gold, platinum or bismuth or their alloys, preferably silver.

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(54) **PRINTED CIRCUIT BOARD MANUFACTURE**

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(*) Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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(58) **Field of Search** 427/96, 97, 98, 427/125, 304, 307, 421, 437, 443.1; 106/1.23-1.28; 208/85; 29/825, 832

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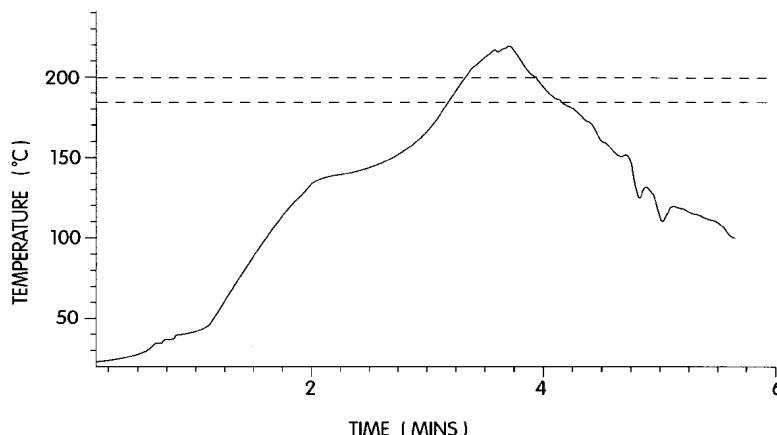
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(57) **ABSTRACT**

A process used during manufacture of printed circuit boards comprises protecting metal pads and/or through-holes to provide a tarnish-resistant and solderable coating. In the method, the pads and/or through-holes are bright-etched, metal plated, preferably by an immersion process, and treated with a tarnish inhibitor. The tarnish inhibitor may be incorporated into the immersion plating bath. The metal plating is usually with silver or bismuth and the pads and/or through-holes comprise copper.

14 Claims, 1 Drawing Sheet



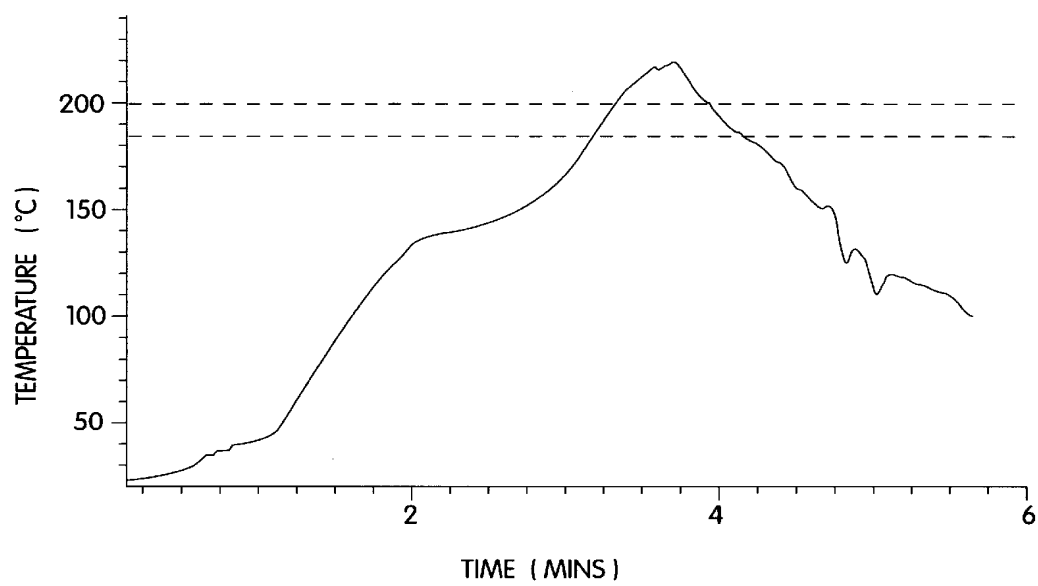


Fig. 1

PRINTED CIRCUIT BOARD MANUFACTURE

This application is a continuation of application Ser. No. 08/567,885, filed Dec. 8, 1995 now abandoned.

FIELD OF THE INVENTION

In the production of a printed circuit board (PCB), in a first (multi-step) stage a "bare board" is prepared and in a second (multi-step) stage, various components are mounted on the board. The present invention relates to the final steps in the manufacture of the bare board, in which the bare board is coated with a protective layer prior to passing to the second production stage.

PRIOR ART

There are currently two types of components for attachment to the bare boards in the second stage referred to above: legged components e.g. resistors, transistors, etc., and, more recently, surface mount devices. Legged components are attached to the board by passing each of the legs through a hole in the board and subsequently ensuring that the hole around the leg is filled with solder. Surface mount devices are attached to the surface of the board by soldering with a flat contact area or by adhesion using an adhesive.

In the first stage referred to above, a board comprising an insulating layer, a conducting circuit pattern and conductive pads and/or through-holes is produced. The board may be a multi-layer board having more than one conducting circuit pattern positioned between insulating layers or may comprise one insulating layer and one conducting circuit pattern.

The through-holes may be plated through so that they are electrically conducting and the pads which form the areas to which the surface mount components will be attached in the subsequent component-attachment stage, are also electrically conducting.

The conductive areas of the circuit pattern, pads and through-holes may be formed from any conductive material or mixtures of different conductive materials. They are generally however, formed from copper. Since over time copper tends to oxidise to form a copper oxide layer with poor solderability, prior to passing to the second, component-attachment stage, a protective layer is coated over the pads and/or through-hole areas where it is desired to retain solderability to prevent formation of a poorly solderable surface layer of copper oxide.

While there is more than one way for preparing the bare boards, one of the most widely used processes for making the bare boards is known as the "solder mask over bare copper" (SMOBC) technique. Such a board generally comprises an epoxy-bonded fiberglass layer clad on one or both sides with conductive material. Generally, the board will be a multi-layer board having alternate conductive layers which comprise circuit pattern, and insulating layers. The conductive material is generally metal foil and most usually copper foil. In the SMOBC technique, such a board is obtained and holes are drilled into the board material using a template or automated drilling machine. The holes are then "plated through" using an electroless copper plating process which deposits a copper layer on the entirety of the board: both on the upper foil surfaces and on the through-hole surfaces.

The board material is then coated with a light sensitive film (photo-resist), exposed to light in preselected areas and chemically developed to remove the unexposed areas revealing the conductive areas which are the plated through-holes and pads. Generally, in the next step, the thickness of the

metal foil in the exposed areas is built up by a further copper electroplating step. A protective layer of an etch resist, which is usually a tin lead alloy electroplate composition is applied over the exposed and thickened copper areas.

The photo-resist is then removed exposing the copper for removal and the exposed copper surface is etched away using a copper etching composition to leave the copper in the circuit pattern finally required. In the next step, the tin-lead alloy resist is stripped away.

Since components will not be attached to the copper circuit traces, it is generally only necessary to coat the solder for attaching the components over the through-hole and pad areas but not the traces. Solder mask is therefore applied to the board to protect the areas where the solder coating is not required, for example using a screen printing process or photo-imaging technique followed by development and, optionally curing. The exposed copper at the holes and pads is then cleaned and prepared for solder coating and the protective solder coating subsequently applied, for example by immersion in a solder bath, followed by hot air leveling (HAL) to form a protective solder coating on the areas of copper not coated with solder mask. The solder does not wet the solder mask so that no coating is formed on top of the solder mask protected areas.

At this stage, the board comprises at least one insulating layer and at least one conductive layer. The conductive layer or layers comprise a circuit trace. The board also comprises a pad or pads and/or through-hole(s) protected from tarnishing by a layer of solder. A single conductive layer may comprise either a circuit trace or pad(s), or both. Any pads will be part of a conductive layer which is an outerlayer of a multi-layer board. The circuit traces on the board are coated with solder mask.

Such a board is ready to proceed to the second stage for attachment of the components. In this second stage, generally attachment of the components is achieved using solder: firstly a layer of solder paste (comprising solder and flux) is applied onto the boards, generally by printing and the components are positioned on the printed boards. The board is then heated in an oven to produce fusion of the solder in the solder paste, which forms a contact between the components and the board. This process is known as reflow soldering. Alternatively a wave soldering process is used in which the board is passed over a bath of molten solder. In either case additional solder is used over and above any protective solder coating.

The additional complications of attaching both legged components and the surface mount devices and the special requirements for mounting many small closely spaced components have resulted in increased demands on the surface protection coating for the conductive metal to which the components will be attached on the PCB's. It is essential that the finish applied by the bare board manufacturer does not leave a pad with an uneven surface as this increases the risk of electrical failure. It is also essential that the protective coating does not interfere with the subsequent solder step, thereby preventing formation of a good, conducting bond between the bare board and components. An extra step in which the protective coating is removed would be undesirable.

As explained above, the conductive metal surfaces are generally formed of copper and the protective surface must be applied at the end of the first stage to prevent the formation of non-solderable copper oxide on the copper surfaces prior to the component attachment. This is particularly important because, generally speaking, the first stage

and the second, component-attachment stage will be carried out at completely different sites. There may therefore be a considerable time delay between formation of conducting pads and/or through-holes and the component-attachment stage, during which time oxidation may occur. Therefore, a protective coating is required which will retain the solderability of conducting material and enable a soldered joint to be made when the components are attached to the bare boards.

The most common protection coating presently used is tin/lead solder, generally applied using the "HAL" (hot air leveling) process, an example of which is described in detail above.

HAL processes are limited because it is difficult to apply the solder evenly and the thickness distribution produced by the use of HAL processes makes it difficult to reliably attach the very small and closely spaced components now being used.

Several replacement treatments for the HAL coating of a solder layer are being introduced. The coatings must enable formation of a reliable electrical contact with the component. They should also be able to stand up to multiple soldering steps. For example, as described above, there are now both legged and surface mount components for attachment to the bare boards and these will generally be attached in at least two soldering operations. Therefore, the protective coatings must also be able to withstand at least two soldering operations, so that the areas to be soldered in a second operation remain protected during the first operation.

Alternatives to the tin/lead alloy solder used in the HAL process, which have been proposed include organic protection, immersion tin or tin/lead plating and nickel/gold plating. In the nickel/gold process electroless plating of the copper surfaces is carried out in which a primer layer of nickel is applied onto the copper followed by a layer of gold. This process is inconvenient because there are many process steps and in addition, the use of gold results in an expensive process.

Organic protection for the copper pads during storage and assembly prior to soldering have also been effected using flux lacquer. Its use is generally confined to single-sided boards (i.e. boards which have conductive pads on only one side). The coating is generally applied by dip, spray or roller coating. Unfortunately, it is difficult to provide a consistent coating to the board surfaces so limited life expectancy, due to the porosity of the coating and to its inconsistent coating thickness, results. Flux lacquers have also been found to have a relatively short shelf life. A further problem is that in the component-attachment stage, if reflow soldering is to be used to attach the components, the components are held in place on the underside of the boards with adhesive. In cases where the flux lacquer is thick, the adhesive does not bond the component directly to the printed board, but instead forms a bond between the adhesive and the lacquer coating. The strength of this bond can drop during the fluxing and soldering step causing components to be lost during contact with the solder baths.

One other alternative currently being used is passivation/protection treatment based upon the use of imidazoles or triazoles in which copper-complex compounds are formed on the copper surface. Thus, these coatings chemically bond to the surface and prevent the reaction between copper and oxygen. However this process is disadvantageous because it tends to be inadequate for withstanding successive soldering steps so that the high temperatures reached in a first soldering step tend to destroy the layer which cannot withstand a

subsequent soldering operation needed to mount further components. One example of such a process is given in EP-A-0428383, where a process is described for the surface treatment of copper or copper alloys comprising immersing the surface of copper or copper alloy in an aqueous solution containing a benzimidazole compound having an alkyl group of at least 3 carbon atoms at the 2-position, and an organic acid.

Processes are also known which provide coatings using compositions which comprise silver.

The three common complexing systems for electroless silver plating processes are either ammonia-based, thiosulphate-based or cyanide-based.

The ammonia systems are disadvantageous because the ammonia-containing silver solutions are unstable and explosive azides may tend to form. Thiosulphate systems are disadvantageous for use in the electronics industry because sulphur compounds in the silver coatings formed result in poor solderability so that in the subsequent component-attachment step, a poor electrical contact may be formed between the bare board and the component.

The cyanide-based systems are disadvantageous due to the toxicity of the plating solutions.

In U.S. Pat. No. 5,318,621 an electroless plating solution containing amino acids as rate enhancers for depositing silver or gold onto a nickel coating overlying copper on a circuit board is disclosed. It is described that neither gold nor silver electroless plating baths based on thiosulphate/sulphate will plate directly onto copper because the copper rapidly dissolves without allowing a silver or gold coating to form. In the introduction of the reference, "Metal Finishing Guidebook & Directory" (1993 edition), silver plating solutions comprising silver nitrate, ammonia and a reducing agent such as formaldehyde are mentioned.

U.S. Pat. No. 4,863,766 also discloses electroless silver plating, using a cyanide-based plating solution. In Metal Finishing (1983) 81(i), pp 27-30 Russev described immersion silvering of copper powder from a plating solution containing silver nitrate and a nitrogen complexing agent. In Metal Finishing (1960) August, p 53 Geld described a silver coating process involving an initial bright dip of the brass or copper substrate, followed by a silver plating step in which a thick coating of silver is plated from a solution of silver nitrate and potassium iodide. The process is for plating of electrical contacts to increase conductivity.

In JP-A-04-110474 a base material is plated with silver, dried and subsequently treated with a mercaptan compound to prevent tarnish.

In DE-C-4316679 base metals such as copper are coated with palladium in a two-step process including a first step in which the surface is contacted with a bath containing a palladium salt and an oxidizing agent, and in the second step with a bath containing a palladium salt, a complexing agent and formic acid or formic acid derivative. The latter bath may also contain stabilizers for the bath itself, which stabilize the bath against decomposition or "plating-out". It is suggested that the copper substrate should previously be etched using a non-bright etch bath including persulphate. However, such pretreatment steps tend to produce relatively porous coatings. The inventors there minimize the porosity of the coating by using the two-step process in the first of which a very thin coating is formed. This reference warns against using silver as corrosion protection due to migration.

The present invention relates to a displacement immersion metal plating in which a more electropositive metal displaces a less electropositive metal at the surface to be coated.

Ions of the more electropositive metal oxidize the substrate metal. A displacement plating process differs from an electroless process because the silver coating forms on the surface of a metal by a simple displacement reaction due to the relative electrode potentials of the oxidisable metal of the surface to be protected and of the silver ions respectively.

It is reported in for example "Modern Electroplating" by F. A. Lowenheim, published by J. Wiley & Sons (1963) that silver will plate by displacement on most base metals but that immersion plated silver is poorly adherent. F. A. Lowenheim there suggests that when electroplating base metals with silver, it is necessary to deposit first a thin film of silver on the work piece from a high-cyanide strike bath to ensure good adhesion of the subsequent electroplated silver layer.

SUMMARY OF THE INVENTION

The present invention aims to provide an alternative to the solder protection coating for the copper or other conducting surfaces of bare boards which require protection from tarnishing between bare board manufacture and the component-attachment stage.

In accordance with the present invention, there is provided a method for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the process comprising contacting the pads and/or through-holes with a bright-etch composition in a bright-etch step; and subsequently immersion plating the etched pads and/or through-holes in a metal-plating step to form solderable plated metal surfaces.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical representation illustrating an example described in the present application.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The insulating layer and conducting layer of the PCB will be as described immediately above. They may comprise the insulating layer and conducting circuit pattern of any conventional PCB, respectively. The pads and/or through-holes for plating are those areas of the PCB for which solderability must be maintained for attachment of components in the subsequent soldering steps for component attachment.

The bright-etch step comprises contacting the pads and/or through-holes with a bright-etch composition. Such compositions are already known in the industry for other applications and they produce a bright smooth cleaned surface on the conducting metal from which the pads and/or through-holes are formed. In contrast, non-bright etch compositions, such as those which are based on persulphate provide microroughened, cleaned surfaces. The use of the bright-etch step allows the formation of a dense, nonporous metal coating, which is particularly suitable for a subsequent soldering step.

Suitable bright-etch compositions are generally aqueous and may be based for example on one or mixtures of more than one of hydrogen peroxide, sulphuric acid, nitric acid, phosphoric acid or hydrochloric acid. The bright-etch compositions generally include at least one component which will tend to modify the dissolution of copper in bright-etch compositions.

Particularly preferred bright-etch compositions where the metal surface of the pads and/or through-holes comprises copper or a copper alloy are, for example, as described in JP

62-188785 A2 (comprising 5.1–10.2 moles/l nitric acid, 4.6–9.2 moles/l sulphuric acid, 0.01 moles/l zinc nitrate and 0.4 moles/l copper nitrate in aqueous solution); JP 60-190582 (comprising for example 20–50% by weight sulphuric acid (96%), 10–25% by weight nitric acid (67.5%), 0.5–1% by weight hydrochloric acid (35%) and 0.5–1% by weight nonionic surfactant); U.S. Pat. No. 3,668, 131 (comprising hydrogen peroxide, sulphuric acid and urea additives); Metal Finishing (February 1986), 84, (2), 67–70 (comprising sodium dichromate, sulphuric acid, hydrochloric acid, sodium diethyldithio carbonate); Trans Inst. Metal Finishing (Summer 1983), 61, (2), 46–49 (acidified hydrogen peroxide comprising hydrogen peroxide, sulphuric acid and stabilizer); Oberflache Surf. (August 1979) 20, (8), 178–179 (comprising nitric acid and dodecyl pyridinium chloride); U.S. Pat. No. 4,510,018 (comprising sulphuric acid, hydrogen peroxide, fatty acid amine and ammonium compound); U.S. Pat. No. 4,459,216 (comprising 5–100 g/l hydrogen peroxide and 100–300 g/l sulphuric acid and aromatic stabilizer); JP 84-038308 (comprising 0.15–0.3 moles/l hydrochloric acid; 0.2–0.4 moles/l phosphoric acid and 0.02–0.1 moles/l sulphuric acid). Where the conducting material of the pads and/or through-holes comprises stainless steel, particularly preferred bright-etch compositions may be as described for example in WO 93-08317; JP 62-238379 A2; DE 1928307; or Tr. Gos. Nauchno-Issled. Proektn. Inst. Osnovn. Khim (1974), 36, 93–97. Where the conducting material is aluminium, a suitable bright-etch is as described in Met. Finishing (July 1986) 84, (7), 55–59.

Thus, any etch composition which provides a bright, cleaned surface may be used. In the bright-etch step, contact with the bright-etch composition may be by immersion, spray or any other coating technique, such as is described in any of the references above, for sufficient time and at a suitable temperature to enable a bright surface to form on the conducting material of the pads and/or through-holes. Generally the temperature for contact with the bright-etch composition will be ambient and the contact time will be from 5 seconds to 10 minutes, preferably at least 30 seconds, or even at least 2 minutes, and preferably for no greater than 5 minutes.

Generally after the etching step, there will be a post-rinse step comprising rinsing with deionized water and generally without drying, the bare boards then proceed directly to the plating step. Alternatively, an acid rinse step may be included, after the aqueous rinse.

The plating step is an immersion (or displacement) plating step. In an immersion plating step, the plating composition comprises metal ions of a metal which is more electropositive than the conducting material. The choice of metal ions in the immersion plating solution, therefore depends on the metal to be plated. Since the pads or through-holes generally comprise copper or nickel, suitable examples of plating metals include bismuth, tin, palladium, silver and gold; silver and bismuth ions are particularly preferred.

A particularly preferred immersion silver plating method is described in our copending British application filed on even date herewith under the application Ser. No. 9425030.5, and subsequent U.S. Ser. No. 08/932,392 now U.S. Pat. No. 5,855,141.

As sources of plating metal ions, any water soluble metal salt may be used, for example nitrates, acetates, sulphates, lactates or formates. Preferably silver nitrate is used.

The metal plating ions are generally in the plating composition at a concentration of from 0.06 to 32 g/l (based on metal ions), preferably from 0.1 to 25 g/l, most preferably from 0.5 to 15 g/l.

Contact of the metal surface with the plating solution will generally be at temperatures of from 10 to 90° C., preferably 15 to 75° C., more preferably 20 to 60° C. For example, the temperature of contact with the plating solution will be from 15 to 50° C., most usually from 20 to 40° C.

Contact can be by any method, usually dip, spray or horizontal immersion coating. Spray coating is preferred. Such contact may be part of a substantially continuous coating process.

The contact time of the plating solution with the metal surface is sufficient to form plated metal surfaces over the metal. Generally the contact time will be from 10 seconds to 10 minutes. A contact time of less than 10 seconds has generally been found to give insufficient coverage with silver coating and although the contact time may be longer than 10 minutes, no additional benefit has been found from a contact time of longer than 10 minutes.

The preferred plating process is an immersion displacement process and not a true electroless plating process. In the preferred plating compositions of the present invention, metal atoms on the surface of the metal are oxidized by the metal plating ions in the solution, so that a layer of plated metal deposits on the pads and/or through-holes. The process is self-limiting because when plated metal covers all of the surface sites of metal oxidizable by the plating metal no further reaction and therefore no further deposition occurs.

In a second aspect of the invention, there is provided for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising metal plating the etched pads and/or through-holes by contact with a plating composition in a metal plating step to form solderable plated metal surfaces and contacting the plated metal surfaces with a solution of a tarnish inhibitor.

In this aspect of the invention, preferably, prior to contacting the metal surface with the plating composition in the plating step, the metal surface is cleaned. Cleaning may be using an acidic cleaning composition, such as any cleaning composition known in the art. Examples are copper conditioner PC 1144 supplied by Alpha Metals Limited of the United Kingdom. Where there is a cleaning step using an acidic cleaning solution, generally there will be a rinsing step prior to contacting the metal surface with the plating solution. Preferably any precleaning will include a bright-etch step. In both aspects of the invention, the tarnish inhibitor may be present in the plating solution itself so that the plating solution comprises the solution comprising tarnish inhibitor. Thus, in a preferred method of the invention, the plated metal surfaces are contacted with a solution comprising a tarnish inhibitor during the plating step (i.e., contact may be during formation of the plated metal surfaces).

Alternatively, the metal surfaces are formed in the plating step and subsequently the formed metal surfaces are contacted with a solution comprising a tarnish inhibitor in a further step. The solution is preferably aqueous, being made up from deionized or otherwise purified water. The composition comprising tarnish inhibitor may additionally comprise solubilizers, for example non-aqueous solvents, surfactants and/or pH buffers.

Contact of the composition comprising tarnish inhibitor with the plated metal surfaces will be for at least 5 seconds, preferably for at least 20 seconds. Where the tarnish inhibitor is present in the plating solution, the time of contact is generally determined by the duration of the plating step.

Generally, the contact time will be from 1 to 5 minutes. The temperature of contact is most usually from 10 to 90° C., preferably 15 to 75° C., more preferably 20 to 60° C. For example the temperature of contact with the plating solution may be from 15 to 50° C., most usually from 20 to 40° C. Contact may be any conventional means, for example by dip, spray or horizontal immersion coating.

The most appropriate pH depends to some extent on the particular tarnish inhibitor used but primarily on the metal ions present in a plating bath which contains the tarnish inhibitor. Where the tarnish inhibitor is contacted in a separate step with the plated metal surface, the pH should be appropriate for the tarnish inhibitor and selected so that it does not attack the plating. Where the solution is a silver plating composition, a convenient pH is in the range of 3 to 10. Where the solution is a bismuth plating composition, the pH may be 1 or lower.

The solution comprising the tarnish inhibitor may be a final rinse solution, applied to the boards prior to drying of the boards. The board may undergo subsequent treatment steps after contact with the composition comprising tarnish inhibitor. However, generally, after contact with the solution, comprising a tarnish inhibitor and drying, they are at the end of the first bare board manufacturing stage, and are ready for the second component-attachment stages. Optionally, for example, there may be a deionized water rinse step, prior to drying.

The concentration of tarnish inhibitor in the solution comprising tarnish inhibitor, will generally be from 0.0001 to 5% by weight, i.e. 0.001 to 50 g/l. Preferably, the amount of tarnish inhibitor will be from 0.005 to 3% by weight, and most preferably from 0.01 to 2% by weight, or even below 1% by weight.

The method of the second aspect of the invention may surprisingly also be used on precious metals such as gold, platinum or ruthenium where it will improve solderability.

In the second aspect of the invention, the metal plating step is preferably an immersion/displacement plating or electroless plating step. It consists of a single step using a single plating composition. Most preferably the plating step will be an immersion/displacement plating step comprising contacting the metal of the pads and/or through-holes with an immersion plating composition.

Where the plating is other than by the preferred immersion/displacement process, for example, if it is by electroless plating, the plating composition may comprise alternative plating metal ions, such as nickel.

The use of tarnish inhibitor in the invention has been found to provide metal coatings which have good tarnish resistance (resistance to humidity and oxidation) even when stored at 40° C. and 93% RH for 96 hours or at 150° C. for 2 hours. The porosity inherent in immersion coatings is reduced by the provision of a level surface using the bright-etch step and using, so that the anti-tarnish properties are considerably improved, even at the high temperatures reached in reflow soldering processes. Concern over the use of silver plating as described for example in DE-C-4316679 due to migration of silver ions is overcome as it has been found that the present invention substantially prevents silver migration by providing a barrier to moisture.

In both the above aspects of the invention, an immersion plating composition preferably contains a complexing agent for the ions of the more electropositive metal.

In a further aspect of the present invention there is provided a displacement metal plating process in which a relatively less electropositive base metal is plated with a

relatively more electropositive coating metal by contact with an aqueous plating composition containing ions of the more electropositive metal, a completing agent for such ions and a tarnish inhibitor for the more electropositive metal so as to form a coating of the more electropositive metal.

In this aspect of the invention there is also provided a new plating composition containing ions of a metal which can be displacement plated, a complexing agent for the ions, preferably present in higher than equimolar amounts as compared to the metal ion, and containing a tarnish inhibitor for the metal, and being substantially free of reducing agent capable of reducing the ions to the metal.

This aspect of the invention has been found to be particularly useful for silver or bismuth plating. Therefore preferably, the plating composition described contains silver or bismuth ions.

The plating composition used in this aspect of the invention may be a immersion plating composition based on any plating composition used in the PCB industry.

In this embodiment of the invention, preferably, prior to contacting the metal surface with the plating composition in the plating step, the metal surface is cleaned. Cleaning may be accomplished using an acidic cleaning composition, such as any cleaning composition known in the art. Examples are copper conditioner PC 1144 supplied by Alpha Metals Limited.

Where there is a cleaning step using an acidic cleaning solution, generally there will be a rinsing step prior to contacting the metal surface with the plating solution.

Preferably any pre-cleaning will include a bright-etch step.

The plating composition may also comprise a complexing agent. If so, the complexing agent is preferably present in an amount of from 0.1 to 250 g/l, preferably from 2 to 200 g/l and most preferably from 10 to 100 g/l, especially around 50 g/l. The complexing agent may be any complexing agent for the plating metal ions which does not form a water insoluble precipitate under the aqueous and pH conditions of the composition. Mixtures of complexing agents may also be used. It is desirable to use complexing agents which are bi-dentate or higher dentate ligands since the stability constants of such complexes are higher than mono-dentate ligands.

Examples of suitable complexing agents have oxygen-containing ligands, for instance amino acids and their salts, preferably having at least 2 and up to 10 carbon atoms, polycarboxylic acids, usually amino acetic acids, such as nitrilo-triacetic acid or, usually, alkylene polyamine poly-acetic acids including ethylene diamine tetra-acetic acid (EDTA), diethylene triamine penta-acetic acid, N-hydroxyethyl ethylene diamine triacetic acid, 1,3-diamino-2-propanol-N,N,N',N'-tetra-acetic acid, bishydroxyphenylethylene diamine diacetic acid, diamino cyclohexane tetra-acetic acid or ethylene glycol-bis-[(β -aminoethylether)-N,N'-tetra-acetic acid]] and N,N,N',N'-tetrakis-(2-hydroxypropyl) ethylene diamine, citrates and/or tartrates, N,N-di-(hydroxyethyl)glycine, gluconates, lactates, citrates, tartrates, crown ethers and/or cryptands.

Particularly preferred complexing agents for silver are EDTA, DTPA and N,N,N',N'-tetrakis-(2-hydroxypropyl) ethylene diamine. The complexing agent should form a soluble complex with plating metal ions in aqueous solution under the pH conditions of the plating solution.

A suitable complexing agent for bismuth is chloride, and it is generally unnecessary to use a multidentate (i.e., bi- or higher dentate) ligand complexing agent for bismuth.

The complexing agent is preferably used either in stoichiometric equivalent amounts or in a stoichiometric excess so that all the plating metal ions may be complexed. By stoichiometric we mean equimolar. Preferably the complexing agent is present in a higher molar concentration than the silver ions, the molar ratio preferably being (at least 1.2):1, more preferably (at least 2.0):1, more preferably (at least 3):1.

Suitable tarnish inhibitors for use in all aspects of the present invention include for example:

- (a) fatty acid amines, preferably having at least 6 carbon atoms, most preferably at least 10 carbon atoms and generally no greater than 30 carbon atoms, they may be primary, secondary, tertiary, diamines, amine salts, amides, ethoxylated amines, ethoxylated diamines, quaternary ammonium salts, quaternary diammonium salts, ethoxylated quaternary ammonium salts, ethoxylated amides and amine oxides. Examples of the primary, secondary and tertiary amine-type corrosion inhibitors are ARMEENTM to (denotes trademark). Examples of the subsequent amine-type corrosion inhibitors are respectively DUOMEENTM, ARMACTM/DUOMAC, ARMIDTM, ETHOMEENTM, ETHODUONEENTM, ARQUADTM, DUOQUADTM, ETHOQUADTM, ETHOMIDTM, AROMOXTM, all supplied by Akzo Chemie.
- (b) purines and substituted purines.
- (c) N-acyl derivatives of sarcosine, such as the SARKO-SYrange of products supplied by Ciba-Geigy.
- (d) organic polycarboxylic acids such as Reocor 190 supplied by Ciba-Geigy.
- (e) substituted imidazoline in which substituents are for example hydroxyl C₁₋₄ alkyl amino or carbonyl-containing groups. Examples include AMINE 0, produced by Ciba-Geigy, especially in combination with a N-acyl sarcosine of category (c).
- (f) alkyl or alkyl benzyl imidazoles, e.g. undecyl imidazole in which the alkyl group has up to 22 carbon atoms, preferably no greater than 11 carbon atoms and in which the alkyl or benzyl groups are optionally substituted.
- (g) benzimidazoles, especially alkylaryl benzimidazoles in which the alkyl group has up to 22 carbon atoms, preferably no greater than 10 carbon atoms and in which the alkyl or benzyl groups are optionally substituted, for example 2-(p-chlorobenzyl) benzimidazole which is particularly preferred.
- (h) phosphate esters such as EKCOL PS-413, supplied by Witco.
- (i) optionally substituted triazole derivatives such as REOMET 42, supplied by Ciba-Geigy. Examples are benzo triazole, tolyl triazole and alkyl substituted triazole derivatives having a carbon number on the alkyl group of from 1 to 22, preferably from 1 to 10.
- (j) substituted tetrazoles, such as 5(3(trifluoromethyl phenyl)) tetrazole, is also a preferred example.

The choice of tarnish inhibitor will depend to some extent upon the metal of the plated metal surfaces, but this will be clear to a person skilled in the art. For example, if the tarnish inhibitor is to be incorporated into a gold plating bath, the tarnish inhibitor may be a chloride salt, however, in contrast, using a silver plating bath, chloride salts may not be used as they will result in formation of an insoluble silver chloride precipitate.

The tarnish inhibitor is preferably water soluble so that the solution is an aqueous solution. However, water immis-

cible tarnish inhibitors may be used although it may be necessary to include a surfactant/cosolvent in the solution.

This invention has been found to provide considerable advantages in preventing tarnishing and conferring humidity resistance on the bare boards produced to that additional protection is provided between the bare board manufacture stage and the component-attachment stage. Solderability is found to be enhanced.

A suitable pH for a silver plating composition may be from 2 to 12, but is preferably from 4 to 10. Thus, the composition may be acidic, up to pH 7. Alternatively, the composition may be alkaline, and have a pH of greater than 7, or even greater than 7.5. A bismuth plating solution usually has a low pH of 1 or less.

A buffering agent may be included in the plating composition to ensure that the pH of the composition is within the desired range. As the buffering agent, any compatible acid or base may be included. A compatible acid or base is an acid or base which in the amounts required in the composition does not result in the precipitation out of solution of the silver ions and/or complexing agent. For example hydrogen chloride is unsuitable for a silver plating composition as it forms an insoluble silver chloride precipitate. Suitable examples include sodium or potassium hydroxide or a carbonate salt, or where acids are required, suitable acids may include citric acid, nitric acid or acetic acid. Borates, phthalates, acetates, phosphonates may be used but the buffer should not result in precipitation of the metal salts and preferably does not inhibit the plating rate. An appropriate buffer will be dependent on the desired working pH.

The plating composition may include optional ingredients such as surfactants or wetting agents to improve the coating uniformity. Where surfactants are included, preferably they are introduced into the composition in an amount such that in the plating bath, they will be present at a concentration of from 0.02 to 100 g/l. Preferably they will be incorporated at a concentration of from 0.1 to 25 g/l and most preferably at a concentration of from 1 to 15 g/l. Any standard surfactant or wetting agent useful in a plating bath may be used. Nonionic surfactants are preferred. Particularly preferred surfactants are alkyl phenol ethoxylates, alcohol ethoxylates and phenol ethoxylates such as *Synperonic NP9 (ex. ICI), *Synperonic A14 (ex. ICI) and *Ethylan HB4 (ex. Harcros), respectively (*denotes trade name).

A further optional ingredient which can be included in the plating baths of the present invention are grain refiners. Grain refiners improve the appearance of the plated metal surfaces by causing formation of smaller crystals of plated metal having a more densely packed structure. Suitable examples of grain refiners include lower alcohols such as those having from 1 to 6 carbon atoms, for example isopropanol and polyethylene glycols, for example PEG 1450 (Carbowax* Union Carbide). Grain refiners may be incorporated in the composition in amounts from 0.02 to 200 g/l. More preferably, if a grain refiner is included, it will be at concentrations of from 0.05 to 100 g/l and most preferably from 0.1 to 10 g/l. Any nonaqueous solvent should be present in amounts below 50% by weight of the composition, preferably below 30% by weight or even below 10% or 5% by weight of the plating composition.

Other non-active, non-interfering components may be included such as defoamers especially for spray applications (e.g., A100 supplied by Dow), dyes, etc.

The balance in the composition is water. Deionized water or other purified water which has had interfering ions removed, is used in the plating composition used in the process of the invention.

In order to form the plating composition for use in the processes of the present invention, preferably a solution is firstly prepared comprising deionized water, complexing agent as defined above, and any buffering agent, optionally with the other optional ingredients, and a salt of the more electropositive metal is added as an aqueous solution to the other components which have been formed into a pre-mix. It has been found that this is the most advantageous way to prepare the solution because trying to dissolve the metal salt directly into the plating composition is relatively time consuming and, where the metal is silver, tends to be more vulnerable to photo-reaction which results in precipitation of silver ions out of solution, as a dark precipitate.

Preferably the pH of the composition to which a silver salt is added will be from pH 3 to 10, most preferably from 4 to 8.

The components are mixed until they have substantially dissolved. The use of heat for silver dissolution is disadvantageous because again, it may tend to cause the formation of a dark silver precipitate.

After contact of the bare board with the solution comprising tarnish inhibitor, the board is dried. Preferably, there will be no post-rinse step between contact of the board with the solution and drying.

Drying may be by any means, but is generally using warm air, for example treated metal may be passed through a drying oven.

The coating obtained using the method of the present invention produces a surface which is considerably more uniform and even than that obtained in the conventional HAL processes and, compared with organic protection, the coating is more resistant to soldering operations. Furthermore, the process of this invention is less expensive and simpler than use of the nickel/gold process.

In the subsequent component-attachment stage, the components are soldered onto the plated pads and/or through-holes of the bare board. The metal of the pad(s) and/or through-holes (generally copper) and plating metal, usually silver, and/or the plating metal and solder may tend to intermix. The bond formed with the components has good electrical conductivity and good bond strength.

After component attachment, finished boards having components attached over the plated layer of the present invention, do not suffer joint reliability problems as do those boards formed using a nickel/gold step.

EXAMPLE 1

A composition was prepared in which 50 g EDTA and 20.4 g of solid sodium hydroxide were mixed with sufficient water to dissolve them. A solution comprising 1g silver nitrate in deionized water was subsequently added to the premixture comprising EDTA and sodium hydroxide solution and deionized water was added to 1 litre. Copper double-sided circuit boards, having a variety of surface mount feature and plated through-holes of various diameter were coated with the silver solution using the following procedure.

Boards were chemically brightened in an aqueous solution of 20% v/v H₂O₂ (35%), 0.5% v/v H₂SO₄ (96%), 2.5% 1,4-butanediol for 1 minute. A tap water rinse was then employed, followed by an acid rinse in 10% H₂SO₄ for 1 minute. The boards were given a further water rinse, then immersed in the silver plating solution at 40° C. for 4 minutes. After removal from the bath, the boards were rinsed with water and warm air dried. Copper areas of the board were coated with a bright, even silver deposit.

Coated boards were subjected to three passes through a typical IR silver paste reflow profile (see FIG. 1), then wave

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soldered using NR300, an Alpha Metals VOC free, no clean flux. 100% filling of the plated through-holes with solder was achieved.

Further boards were stored in a humidity cabinet at 40° C./93% RH for 24 hours before being passed through 3 IR reflow profiles. These boards showed a slight degree of tarnishing on the silver coating. However 100% hole filling was still achieved during subsequent wave soldering with NR 300 flux.

EXAMPLE 2

A silver plating solution was prepared by forming a solution comprising 50 g EDTA, 20.4 g NaOH, 14 g Ethylan HB4 (Akros Chemicals), 3 g Crodamet 02 (Croda Chemicals) in 800 mls deionized water. To this solution was added a solution of 1 g AgNO₃ in 100 mls deionized water. The pH was adjusted to 6.8 by addition of dilute NaOH/HNO₃, then made up to 1 litre with deionized water.

Double sided bare copper boards were coated with the above solution using the procedure as described in Example 1. 100% filling of plated through-holes with solder was achieved during wave soldering with NR300 flux after passage through 3 IR reflow profiles.

Boards stored at 40° C./93% RH for 24 hours prior to passage through 3 IR reflow profiles showed no evidence of tarnishing and soldered well during wave soldering trials, giving 100% hole filling.

EXAMPLE 3

Double-sided bare copper boards were coated using the bath composition and procedure as described in Example 1. Following removal of the boards from the silver plating solution and rinsing, the boards were immersed in a solution of 4 g Reomet 42 (Ciba-Geigy) in 1 litre deionized water (pH 7) for 1 minute at room temperature. The boards were then rinsed in tap water and warm air dried. A bright even silver coating was produced.

The coated boards were stored at 40° C./93% RH for 24 hours then passed through 3 IR paste reflow profiles. The boards showed no evidence of tarnishing, and soldered well when wave soldered using KR 300 flux.

EXAMPLE 4

Coupons of copper strip (5 cm×1 cm) were coated with the silver coating as described in Example 2. In addition, further samples were coated with immersion tin, 63/37 Sn/Pb and two competitors solderability preservative coatings based on substituted benzimidazole chemistry. The following coating procedures were applied for the various samples:

Immersion Tin Coating

Coupons were etched in an aqueous solution of Na₂S₂O₈ (5%), H₂SO₄ (5%) for 2 minutes, rinsed with tap water, then rinsed with 10% H₂SO₄, for 1 minute and then rinsed with deionized water. The coupons were then immersed in an immersion tin plating solution comprising 0.33 g/l Sn(BF₄)₂, 150 g/l thiourea, 20 g/l fluoroboric acid and 5 g/l Synparonic NP9 (ex. ICI) in deionized water, for 1 minute at room temperature. The coupons were then rinsed with deionized water and warm air dried.

Sn/Pb Coating

Coupons were etched in an aqueous solution comprising Na₂S₂O₈, (5%) and H₂SO₄ (5%), rinsed with tap water then

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with 10% H₂SO₄ and then with deionized water. The coupons were warm air dried. Alpha NR 300 flux was then applied to each coupon. The coupons were then coated 63/37 Sn/Pb by immersion in molten solder at 250° C. for 3 seconds.

Azole 1 and Azole 2

Coupons were etched and rinsed as for the immersion tin samples. Coupons were then immersed in the solution containing the azole at 40° C. for 90 seconds. After removal from the azole containing solution, the coupons were rinsed with deionized water, and warm air dried.

The coupons were subjected to a variety of different pretreatments.

- A. No pre-treatment.
- B. Passage through 3 solder paste reflow profiles.
- C. Storage at 40° C./93% RH for 96 hours.
- D. Storage at 40° C./94% RH for 96 hours, then 3 solder paste reflow profiles.
- E. Storage at 150° C. for 2 hours.

Samples were then soldered using a meniscograph with NR300 flux.

The meniscograph test method monitors the solderability by measuring the net force acting between specimen and solder. The coatings are assessed by the length of time to reach zero wetting force, and the size of the equilibrium wetting force. To achieve good results in wave soldering a short wetting time and high equilibrium wetting force are preferred.

The table below shows the wetting times in seconds and wetting forces after 2 seconds immersion in mN/mm for various copper coated samples.

As can be seen from above, the silver coatings prepared according to this invention have shorter wetting times and higher wetting forces than the Sn and benzimidazole alternative and retain these properties more readily after humidity and heat treatment.

TABLE 1

Coating	Pre-Treatment	Wet Time/Sec	Wetting Force at 2 Seconds
Example 2	A	0.7	0.429
Example 2	B	0.8	0.444
Example 2	C	0.7	0.429
Example 2	D	0.7	0.441
Example 2	E	0.8	0.438
Tin	A	0.9	0.488
Tin	B	>5	-0.028
Tin	C	>5	0.008
Tin	D	>5	-0.148
Azole 1	A	0.8	0.439
Azole 1	B	0.9	0.412
Azole 1	C	0.9	0.443
Azole 1	D	0.9	0.426
Azole 1	E	1.0	0.421
Azole 2	A	0.9	0.449
Azole 2	B	1.0	0.417
Azole 2	C	0.9	0.466
Azole 2	D	1.1	0.310
Azole 2	E	1.2	0.296
Sn/Pb	A	0.8	0.475
Sn/Pb	B	0.8	0.501
Sn/Pb	C	0.8	0.492
Sn/Pb	D	0.8	0.474
Sn/Pb	E	0.8	0.492

EXAMPLE 5

A displacement bismuth plating composition was prepared comprising 3.9 g bismuth oxide, 183.1 g hydrogen

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chloride (as 37% solution), 490.5 g glycolic acid (70% solution), 265.4 g (50% sodium hydroxide solution), 0.077 g potassium iodide, 0.003 g Synperonic NP9 (ex. ICI) and 4 g 2p-chlorobenzyl benzimidazole, were added to deionized water to make 1 liter of product solution. Bare boards having copper pads and copper through-holes were chemically brightened as described in Example 1, then immersed in the plating baths for 2 minutes at 70° C. A coating of bismuth was formed on the surface of the copper having a thickness of 0.05 μ m. Subsequent solderability and tarnish resistance tests carried out on the plated bare boards showed good results for solderability and tarnish resistance.

EXAMPLE 6

Double-sided bare copper boards were bright etched in an aqueous solution of 50% v/v HNO₃, 10% H₂SO₄, 10% H₃PO₄, 1% HCl for 1 minute at room temperature. Boards were then rinsed in tap water followed by 10% H₂SO₄ for 1 minute. After a further water rinse, boards were immersed in silver plating bath described in Example 2 for 4 minutes at 45° C. Boards were then water rinsed and warm air dried.

The coated boards were stored at 40° C./93% RH for 24 hours then passed through 3 IR paste reflow profiles. The boards showed no evidence of tarnishing when wave soldered using NR 300 flux.

EXAMPLE 7

A silver plating bath was prepared by forming a solution comprising 64.8 g diethylene triamine penta-acetic acid, 23.0 g NaOH, 24 g surfactant Ethylan HB4 (Akros Chemicals), 2.5 g Crodamet 02 an ethoxylated 3° amine compound (Croda Chemicals) in 800 mls deionized water. To this solution was added a solution of 1 g silver nitrate in 100 mls deionized water. The pH of this solution was adjusted to 6.9 by addition of dilute NaOH solution or nitric acid. The volume was then made up to 1 litre using deionized water.

Double-sided bare copper boards were coated using the above solution using the procedure as described in Example 1. 100% filling of the plated through-holes was achieved during wave-soldering of the coated boards using Alpha Metals MR300 flux after passage through 3 IR reflow profiles showed no evidence of tarnishing, and soldered well during wave-soldering trials giving 100% hole-fill.

EXAMPLE 8

An immersion silver plating solution was prepared comprising 98.2 g deionized water, 1 g of nitric acid, 0.1 g of silver nitrate, 0.3 g of Chemeen C2 (antitarnish) and 0.4 g Mazawet DF (solubilizer). The pH was adjusted to 6 using a 50% solution of ethylene diamine. The bath produced an adherent silver deposit on copper coupons which showed good solderability and humidity resistance.

EXAMPLE 9

A bismuth plating solution was prepared containing bismuth trioxide 2.1% weight, hydrochloric acid (22°Be) 46.73% weight, glycolic acid (70%) 49.5% weight, potassium chloride 0.07% weight, polyethylene glycol 600 0.1% weight, Chemax Chemeen C2 0.2% weight, distilled water 1.2% weight and tartaric acid 0.1% weight. A further solution was prepared from which the Chemeen C2 was omitted. Samples of copper clad printed circuit material were plated in each of the solutions. These plated samples were then placed in a humidity chamber for 16 hours at 60° C. and 95% relative humidity.

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After this exposure the samples were examined, and those prepared in the solution without the Chemeen C2 were heavily tarnished. The samples prepared in the solution containing the tarnish inhibitor had a good appearance with minimal oxidation, and when tested showed good solderability.

Other embodiments of the invention are to be considered within the scope of the appended claims.

What is claimed is:

1. A method for coating a printed circuit board having metal pads, metal through-holes or a combination thereof, the metal pads, metal through-holes or the combination thereof being formed of a first metal, the method comprising the steps of:

contacting the metal pads, the metal through-holes or the combination thereof with a bright-etch composition to form etched pads, etched through-holes or a combination thereof, the etched pads, the etched through-holes or the combination thereof being formed of the first metal; and

contacting the etched pads, the etched through-holes or the combination thereof with a plating composition comprising ions of a second metal, the second metal being different from the first metal, and a tarnish inhibitor, the tarnish inhibitor characterized in that it coexists with the second metal in solution, to form a printed circuit board having pads, through-holes or a combination thereof that are formed of the first metal coated by a separate layer of the second metal and by a layer of the tarnish inhibitor.

2. A method according to claim 1, wherein the step of contacting the etched pads, the etched through-holes or the combination thereof with a plating composition includes contacting the etched pads, the etched through-holes or the combination thereof with an aqueous solution including the tarnish inhibitor and the ions of the second metal.

3. A method according to claim 1, wherein the step of contacting the etched pads, the etched through-holes or the combination thereof with a plating composition includes contacting the etched pads, the etched through-holes or the combination thereof with a plating composition that includes a complexing agent for the ions of the second metal.

4. A method according to claim 1, wherein the step of contacting the etched pads, the etched through-holes or the combination thereof with a plating composition includes contacting the etched pads, the etched through-holes or the combination thereof with a plating composition that includes ions of a second metal selected from the group consisting of nickel, silver, tin, lead, palladium, cobalt, gold, platinum, bismuth and combinations thereof.

5. A method according to claim 1, wherein the step of contacting the metal pads, the metal through-holes or the combination thereof with a bright etch composition includes contacting copper coated pads, copper coated through-holes and combinations thereof with the bright etch composition.

6. A method according to claim 1, further comprising a step of applying, to a surface of the printed circuit board, a mask such that the pads, the through-holes or the combination thereof are left exposed.

7. A method according to claim 1, further comprising a step of soldering components to the printed circuit board having the pads, the through-holes or the combination thereof that are formed of the first metal coated by a separate layer of the second metal and by a layer of the tarnish inhibitor.

8. A method according to claim 5, wherein the step of contacting the etched pads, the etched through-holes or the

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combination thereof with a complexing agent for the ions of the second metal includes contacting the etched pads, the etched through-holes or the combination thereof with a multidentate ligand complexing agent of the second metal.

9. A method according to claim 4, wherein the step of contacting the etched pads, the etched through-holes or the combination thereof with a plating composition includes contacting the etched pads, the etched through-holes or the combination thereof with a plating composition in which the ions of the second metal are silver ions.

10. A method according to claim 1, wherein the step of contacting the etched pads, the etched through-holes or the combination thereof with a plating composition includes contacting the etched pads, the etched through-holes or the combination with the plating composition for a time period of from 10 seconds to 5 minutes.

11. A method according to claim 1, wherein the step of contacting the etched pads, the etched through-holes or the combination thereof with a plating composition includes contacting the etched pads, the etched through-holes or the combination thereof with a plating composition in which the

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tarnish inhibitor is present in an amount of from 0.001% to 5% by weight of the plating composition.

12. A method according to claim 1, wherein the electropositivity of the second metal is greater than an electropositivity of the first metal.

13. A method according to claim 1, wherein an insulating layer is disposed beneath the pads, the through-holes or the combination thereof formed of the first metal coated by a separate layer of the second metal and by a layer of the tarnish inhibitor.

14. A method of coating copper areas of a printed circuit board, the method comprising steps of:

contacting the copper areas with a plating composition including silver ions and a tarnish inhibitor, the tarnish inhibitor characterized in that it coexists with the silver in solution, to form areas formed of copper coated by a separate layer of silver and by a layer of the tarnish inhibitor.

* * * * *



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Soutar et al.

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(54) **PRINTED CIRCUIT BOARD MANUFACTURE**

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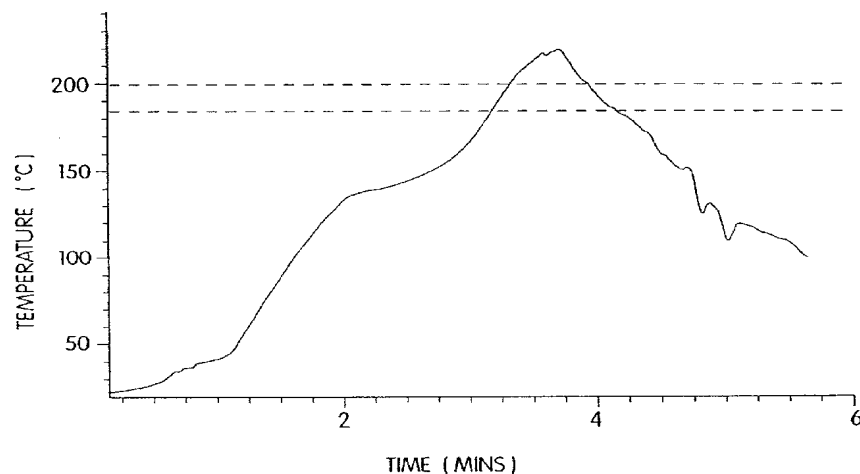
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Glovsky and Popeo, P.C.

(57) **ABSTRACT**

A process used during manufacture of printed circuit boards
comprises protecting metal pads and/or through-holes to
provide a tarnish-resistant and solderable coating. In the
method, the pads and/or through-holes are bright-etched,
metal plated, preferably by an immersion process, and
treated with a tarnish inhibitor. The tarnish inhibitor may be
incorporated into the immersion plating bath. The metal
plating is usually with silver or bismuth and the pads and/or
through-holes comprise copper.

31 Claims, 1 Drawing Sheet



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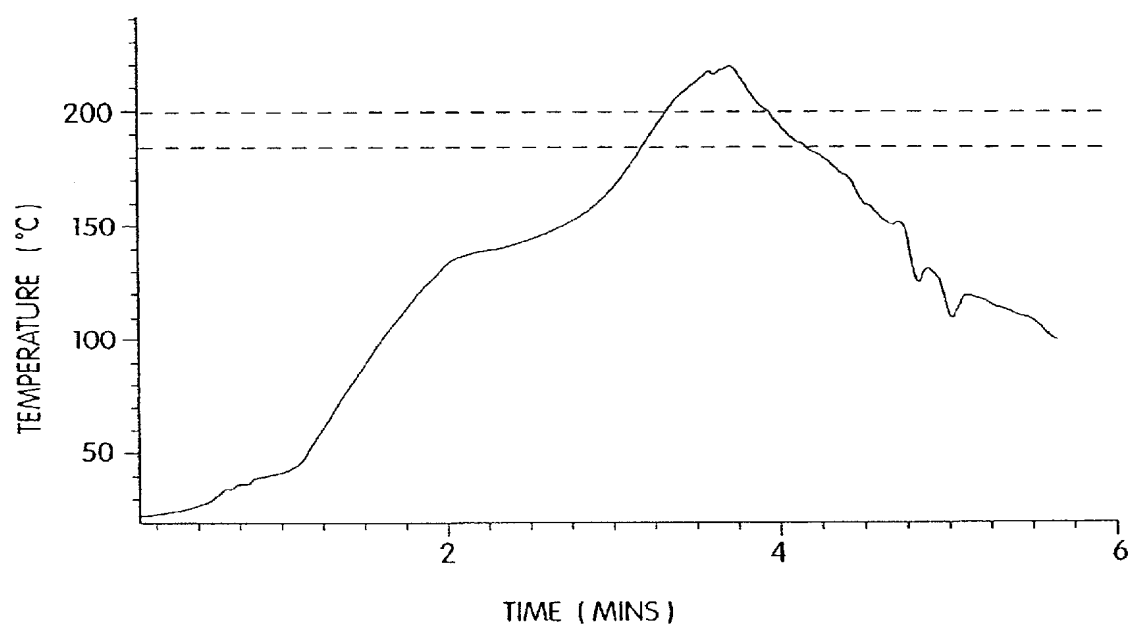


Fig. 1

PRINTED CIRCUIT BOARD MANUFACTURE**RELATED APPLICATIONS**

This application is a continuation of application Ser. No. 08/939,656 (U.S. Pat. No. 6,395,329), filed Sep. 29, 1997, which was a continuation of application Ser. No. 08/567,885 (now abandoned), filed Dec. 8, 1995, which claimed priority to application Serial No. 9425031.3, filed on Dec. 9, 1994, in Great Britain.

FIELD OF THE INVENTION

In the production of a printed circuit board (PCB), in a first (multi-step) stage a "bare board" is prepared and in a second (multi-step) stage, various components are mounted on the board. The present invention relates to the final steps in the manufacture of the bare board, in which the bare board is coated with a protective layer prior to passing to the second production stage.

PRIOR ART

There are currently two types of components for attachment to the bare boards in the second stage referred to above: legged components e.g. resistors, transistors, etc., and, more recently, surface mount devices. Legged components are attached to the board by passing each of the legs through a hole in the board and subsequently ensuring that the hole around the leg is filled with solder. Surface mount devices are attached to the surface of the board by soldering with a flat contact area or by adhesion using an adhesive.

In the first stage referred to above, a board comprising an insulating layer, a conducting circuit pattern and conductive pads and/or through-holes is produced. The board may be a multi-layer board having more than one conducting circuit pattern positioned between insulating layers or may comprise one insulating layer and one conducting circuit pattern.

The through-holes may be plated through so that they are electrically conducting and the pads which form the areas to which the surface mount components will be attached in the subsequent component-attachment stage, are also electrically conducting.

The conductive areas of the circuit pattern, pads and through-holes may be formed from any conductive material or mixtures of different conductive materials. They are generally however, formed from copper. Since over time copper tends to oxidise to form a copper oxide layer with poor solderability, prior to passing to the second, component-attachment stage, a protective layer is coated over the pads and/or through-hole areas where it is desired to retain solderability to prevent formation of a poorly solderable surface layer of copper oxide.

While there is more than one way for preparing the bare boards, one of the most widely used processes for making the bare boards is known as the "solder mask over bare copper" (SMOBC) technique. Such a board generally comprises an epoxy-bonded fiberglass layer clad on one or both sides with conductive material. Generally, the board will be a multi-layer board having alternate conductive layers which comprise circuit pattern, and insulating layers. The conductive material is generally metal foil and most usually copper foil. In the SMOBC technique, such a board is obtained and holes are drilled into the board material using a template or automated drilling machine. The holes are then "plated through" using an electroless copper plating process which deposits a copper layer on the entirety of the board: both on the upper foil surfaces and on the through-hole surfaces.

The board material is then coated with a light sensitive film (photo-resist), exposed to light in preselected areas and chemically developed to remove the unexposed areas revealing the conductive areas which are the plated through-holes and pads. Generally, in the next step, the thickness of the metal foil in the exposed areas is built up by a further copper electroplating step. A protective layer of an etch resist, which is usually a tin lead alloy electroplate composition is applied over the exposed and thickened copper areas.

The photo-resist is then removed exposing the copper for removal and the exposed copper surface is etched away using a copper etching composition to leave the copper in the circuit pattern finally required. In the next step, the tin-lead alloy resist is stripped away.

Since components will not be attached to the copper circuit traces, it is generally only necessary to coat the solder for attaching the components over the through-hole and pad areas but not the traces. Solder mask is therefore applied to the board to protect the areas where the solder coating is not required, for example using a screen printing process or photo-imaging technique followed by development and, optionally curing. The exposed copper at the holes and pads is then cleaned and prepared for solder coating and the protective solder coating subsequently applied, for example by immersion in a solder bath, followed by hot air leveling (HAL) to form a protective solder coating on the areas of copper not coated with solder mask. The solder does not wet the solder mask so that no coating is formed on top of the solder mask protected areas.

At this stage, the board comprises at least one insulating layer and at least one conductive layer. The conductive layer or layers comprise a circuit trace. The board also comprises a pad or pads and/or through-hole(s) protected from tarnishing by a layer of solder. A single conductive layer may comprise either a circuit trace or pad(s), or both. Any pads will be part of a conductive layer which is an outerlayer of a multi-layer board. The circuit traces on the board are coated with solder mask.

Such a board is ready to proceed to the second stage for attachment of the components. In this second stage, generally attachment of the components is achieved using solder: firstly a layer of solder paste (comprising solder and flux) is applied onto the boards, generally by printing and the components are positioned on the printed boards. The board is then heated in an oven to produce fusion of the solder in the solder paste, which forms a contact between the components and the board. This process is known as reflow soldering. Alternatively a wave soldering process is used in which the board is passed over a bath of molten solder. In either case additional solder is used over and above any protective solder coating.

The additional complications of attaching both legged components and the surface mount devices and the special requirements for mounting many small closely spaced components have resulted in increased demands on the surface protection coating for the conductive metal to which the components will be attached on the PCB's. It is essential that the finish applied by the bare board manufacturer does not leave a pad with an uneven surface as this increases the risk of electrical failure. It is also essential that the protective coating does not interfere with the subsequent solder step, thereby preventing formation of a good, conducting bond between the bare board and components. An extra step in which the protective coating is removed would be undesirable.

As explained above, the conductive metal surfaces are generally formed of copper and the protective surface must

be applied at the end of the first stage to prevent the formation of non-solderable copper oxide on the copper surfaces prior to the component attachment. This is particularly important because, generally speaking, the first stage and the second, component-attachment stage will be carried out at completely different sites. There may therefore be a considerable time delay between formation of conducting pads and/or through-holes and the component-attachment stage, during which time oxidation may occur. Therefore, a protective coating is required which will retain the solderability of conducting material and enable a soldered joint to be made when the components are attached to the bare boards.

The most common protection coating presently used is tin/lead solder, generally applied using the "HAL" (hot air leveling) process, an example of which is described in detail above.

HAL processes are limited because it is difficult to apply the solder evenly and the thickness distribution produced by the use of HAL processes makes it difficult to reliably attach the very small and closely spaced components now being used.

Several replacement treatments for the HAL coating of a solder layer are being introduced. The coatings must enable formation of a reliable electrical contact with the component. They should also be able to stand up to multiple soldering steps. For example, as described above, there are now both legged and surface mount components for attachment to the bare boards and these will generally be attached in at least two soldering operations. Therefore, the protective coatings must also be able to withstand at least two soldering operations, so that the areas to be soldered in a second operation remain protected during the first operation.

Alternatives to the tin/lead alloy solder used in the HAL process, which have been proposed include organic protection, immersion tin or tin/lead plating and nickel/gold plating. In the nickel/gold process electroless plating of the copper surfaces is carried out in which a primer layer of nickel is applied onto the copper followed by a layer of gold. This process is inconvenient because there are many process steps and in addition, the use of gold results in an expensive process.

Organic protection for the copper pads during storage and assembly prior to soldering have also been effected using flux lacquer. Its use is generally confined to single-sided boards (i.e. boards which have conductive pads on only one side). The coating is generally applied by dip, spray or roller coating. Unfortunately, it is difficult to provide a consistent coating to the board surfaces so limited life expectancy, due to the porosity of the coating and to its inconsistent coating thickness, results. Flux lacquers have also been found to have a relatively short shelf life. A further problem is that in the component-attachment stage, if reflow soldering is to be used to attach the components, the components are held in place on the underside of the boards with adhesive. In cases where the flux lacquer is thick, the adhesive does not bond the component directly to the printed board, but instead forms a bond between the adhesive and the lacquer coating. The strength of this bond can drop during the fluxing and soldering step causing components to be lost during contact with the solder baths.

One other alternative currently being used is passivation/protection treatment based upon the use of imidazoles or triazoles in which copper-complex compounds are formed on the copper surface. Thus, these coatings chemically bond to the surface and prevent the reaction between copper and

oxygen. However this process is disadvantageous because it tends to be inadequate for withstanding successive soldering steps so that the high temperatures reached in a first soldering step tend to destroy the layer which cannot withstand a subsequent soldering operation needed to mount further components. One example of such a process is given in EP-A-0428383, where a process is described for the surface treatment of copper or copper alloys comprising immersing the surface of copper or copper alloy in an aqueous solution containing a benzimidazole compound having an alkyl group of at least 3 carbon atoms at the 2-position, and an organic acid.

Processes are also known which provide coatings using compositions which comprise silver.

The three common complexing systems for electroless silver plating processes are either ammonia-based, thiosulphate-based or cyanide-based.

The ammonia systems are disadvantageous because the ammonia-containing silver solutions are unstable and explosive azides may tend to form. Thiosulphate systems are disadvantageous for use in the electronics industry because sulphur compounds in the silver coatings formed result in poor solderability so that in the subsequent component-attachment step, a poor electrical contact may be formed between the bare board and the component.

The cyanide-based systems are disadvantageous due to the toxicity of the plating solutions.

In U.S. Pat. No. 5,318,621 an electroless plating solution containing amino acids as rate enhancers for depositing silver or gold onto a nickel coating overlying copper on a circuit board is disclosed. It is described that neither gold nor silver electroless plating baths based on thiosulphate/sulphate will plate directly onto copper because the copper rapidly dissolves without allowing a silver or gold coating to form. In the introduction of the reference, "Metal Finishing Guidebook & Directory" (1993 edition), silver plating solutions comprising silver nitrate, ammonia and a reducing agent such as formaldehyde are mentioned.

U.S. Pat. No. 4,863,766 also discloses electroless silver plating, using a cyanide-based plating solution. In Metal Finishing (1983) 81(i), pp 27-30 Russev described immersion silvering of copper powder from a plating solution containing silver nitrate and a nitrogen complexing agent. In Metal Finishing (1960) August, p 53 Geld described a silver coating process involving an initial bright dip of the brass or copper substrate, followed by a silver plating step in which a thick coating of silver is plated from a solution of silver nitrate and potassium iodide. The process is for plating of electrical contacts to increase conductivity.

In JP-A-04-110474 a base material is plated with silver, dried and subsequently treated with a mercaptan compound to prevent tarnish.

In DE-C-4316679 base metals such as copper are coated with palladium in a two-step process including a first step in which the surface is contacted with a bath containing a palladium salt and an oxidizing agent, and in the second step with a bath containing a palladium salt, a complexing agent and formic acid or formic acid derivative. The latter bath may also contain stabilizers for the bath itself, which stabilize the bath against decomposition or "plating-out". It is suggested that the copper substrate should previously be etched using a non-bright etch bath including persulphate. However, such pretreatment steps tend to produce relatively porous coatings. The inventors there minimize the porosity of the coating by using the two-step process in the first of which a very thin coating is formed. This reference warns against using silver as corrosion protection due to migration.

The present invention relates to a displacement immersion metal plating in which a more electropositive metal displaces a less electropositive metal at the surface to be coated. Ions of the more electropositive metal oxidize the substrate metal. A displacement plating process differs from an electroless process because the silver coating forms on the surface of a metal by a simple displacement reaction due to the relative electrode potentials of the oxidisable metal of the surface to be protected and of the silver ions respectively.

It is reported in for example "Modern Electroplating" by F. A. Lowenheim, published by J. Wiley & Sons (1963) that silver will plate by displacement on most base metals but that immersion plated silver is poorly adherent. F. A. Lowenheim there suggests that when electroplating base metals with silver, it is necessary to deposit first a thin film of silver on the work piece from a high-cyanide strike bath to ensure good adhesion of the subsequent electroplated silver layer.

SUMMARY OF THE INVENTION

The present invention aims to provide an alternative to the solder protection coating for the copper or other conducting surfaces of bare boards which require protection from tarnishing between bare board manufacture and the component-attachment stage.

In accordance with the present invention, there is provided a method for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the process comprising contacting the pads and/or through-holes with a bright-etch composition in a bright-etch step; and subsequently immersion plating the etched pads and/or through-holes in a metal-plating step to form solderable plated metal surfaces.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical representation illustrating an example described in the present application.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The insulating layer and conducting layer of the PCB will be as described immediately above. They may comprise the insulating layer and conducting circuit pattern of any conventional PCB, respectively. The pads and/or through-holes for plating are those areas of the PCB for which solderability must be maintained for attachment of components in the subsequent soldering steps for component attachment.

The bright-etch step comprises contacting the pads and/or through-holes with a bright-etch composition. Such compositions are already known in the industry for other applications and they produce a bright smooth cleaned surface on the conducting metal from which the pads and/or through-holes are formed. In contrast, non-bright etch compositions, such as those which are based on persulphate provide microroughened, cleaned surfaces. The use of the bright-etch step allows the formation of a dense, nonporous metal coating, which is particularly suitable for a subsequent soldering step.

Suitable bright-etch compositions are generally aqueous and may be based for example on one or mixtures of more than one of hydrogen peroxide, sulphuric acid, nitric acid, phosphoric acid or hydrochloric acid. The bright-etch compositions generally include at least one component which will tend to modify the dissolution of copper in bright-etch compositions.

Particularly preferred bright-etch compositions where the metal surface of the pads and/or through-holes comprises copper or a copper alloy are, for example, as described in JP 62-188785 A2 (comprising 5.1–10.2 moles/l nitric acid, 4.6–9.2 moles/l sulphuric acid, 0.01 moles/l zinc nitrate and 0.4 moles/l copper nitrate in aqueous solution); JP 60-190582 (comprising for example 20–50% by weight sulphuric acid (96%), 10–25% by weight nitric acid (67.5%), 0.5–1% by weight hydrochloric acid (35%) and 0.5–1% by weight nonionic surfactant); U.S. Pat. No. 3,668, 131 (comprising hydrogen peroxide, sulphuric acid and urea additives); Metal Finishing (February 1986), 84, (2), 67–70 (comprising sodium dichromate, sulphuric acid, hydrochloric acid, sodium diethyldithio carbonate); Trans Inst. Metal Finishing (Summer 1983), 61, (2), 46–49 (acidified hydrogen peroxide comprising hydrogen peroxide, sulphuric acid and stabilizer); Oberflache Surf. (August 1979) 20, (8), 178–179 (comprising nitric acid and dodecyl pyridinium chloride); U.S. Pat. No. 4,510,018 (comprising sulphuric acid, hydrogen peroxide, fatty acid amine and ammonium compound); U.S. Pat. No. 4,459,216 (comprising 5–100 g/l hydrogen peroxide and 100–300 g/l sulphuric acid and aromatic stabilizer); JP 84-038308 (comprising 0.15–0.3 moles/l hydrochloric acid; 0.2–0.4 moles/l phosphoric acid and 0.02–0.1 moles/l sulphuric acid). Where the conducting material of the pads and/or through-holes comprises stainless steel, particularly preferred bright-etch compositions may be as described for example in WO 93-08317; JP 62-238379 A2; DE 1928307; or Tr. Gos. Nauchno-Issled. Proektn. Inst. Osnovn. Khim (1974), 36, 93–97. Where the conducting material is aluminium, a suitable bright-etch is as described in Met. Finishing (July 1986) 84, (7), 55–59.

Thus, any etch composition which provides a bright, cleaned surface may be used. In the bright-etch step, contact with the bright-etch composition may be by immersion, spray or any other coating technique, such as is described in any of the references above, for sufficient time and at a suitable temperature to enable a bright surface to form on the conducting material of the pads and/or through-holes. Generally the temperature for contact with the bright-etch composition will be ambient and the contact time will be from 5 seconds to 10 minutes, preferably at least 30 seconds, or even at least 2 minutes, and preferably for no greater than 5 minutes.

Generally after the etching step, there will be a post-rinse step comprising rinsing with deionized water and generally without drying, the bare boards then proceed directly to the plating step. Alternatively, an acid rinse step may be included, after the aqueous rinse.

The plating step is an immersion (or displacement) plating step. In an immersion plating step, the plating composition comprises metal ions of a metal which is more electropositive than the conducting material. The choice of metal ions in the immersion plating solution, therefore depends on the metal to be plated. Since the pads or through-holes generally comprise copper or nickel, suitable examples of plating metals include cobalt, bismuth, tin, palladium, silver and gold; silver and bismuth ions are particularly preferred. The plating composition is substantially free of any reducing agent for the ions of the plating metal.

A particularly preferred immersion silver plating method is described in our copending British application filed on even date herewith under the application number 9425030.5, and sequent U.S. Ser. No. 08/932,392 now U.S. Pat. No. 5,955,141.

As sources of plating metal ions, any water soluble metal salt may be used, for example nitrates, acetates, sulphates, lactates or formates. Preferably silver nitrate is used.

The metal plating ions are generally in the plating composition at a concentration of from 0.06 to 32 g/l (based on metal ions), preferably from 0.1 to 25 g/l, most preferably from 0.5 to 15 g/l.

Contact of the metal surface with the plating solution will generally be at temperatures of from 10 to 90° C., preferably 15 to 75° C., more preferably 20 to 60° C. For example, the temperature of contact with the plating solution will be from 15 to 50° C., most usually from 20 to 40° C.

Contact can be by any method, usually dip, spray or horizontal immersion coating. Spray coating is preferred. Such contact may be part of a substantially continuous coating process.

The contact time of the plating solution with the metal surface is sufficient to form plated metal surfaces over the metal. Generally the contact time will be from 10 seconds to 10 minutes. A contact time of less than 10 seconds has generally been found to give insufficient coverage with silver coating and although the contact time may be longer than 10 minutes, no additional benefit has been found from a contact time of longer than 10 minutes.

The preferred plating process is an immersion displacement process and not a true electroless plating process. In the preferred plating compositions of the present invention, metal atoms on the surface of the metal are oxidized by the metal plating ions in the solution, so that a layer of plated metal deposits on the pads and/or through-holes. The process is self-limiting because when plated metal covers all of the surface sites of metal oxidizable by the plating metal no further reaction and therefore no further deposition occurs.

In a second aspect of the invention, there is provided for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising metal plating the etched pads and/or through-holes by contact with a plating composition in a metal plating step to form solderable plated metal surfaces and contacting the plated metal surfaces with a solution of a tarnish inhibitor.

In this aspect of the invention, preferably, prior to contacting the metal surface with the plating composition in the plating step, the metal surface is cleaned. Cleaning may be using an acidic cleaning composition, such as any cleaning composition known in the art. Examples are copper conditioner PC 1144 supplied by Alpha Metals Limited of the United Kingdom. Where there is a cleaning step using an acidic cleaning solution, generally there will be a rinsing step prior to contacting the metal surface with the plating solution. Preferably any pre-cleaning will include a bright-etch step. In both aspects of the invention, the tarnish inhibitor may be present in the plating solution itself so that the plating solution comprises the solution comprising tarnish inhibitor. Thus, in a preferred method of the invention, the plated metal surfaces are contacted with a solution comprising a tarnish inhibitor during the plating step (i.e., contact may be during formation of the plated metal surfaces).

Alternatively, the metal surfaces are formed in the plating step and subsequently the formed metal surfaces are contacted with a solution comprising a tarnish inhibitor in a further step. The solution is preferably aqueous, being made up from deionized or otherwise purified water. The composition comprising tarnish inhibitor may additionally comprise solubilizers, for example non-aqueous solvents, surfactants and/or pH buffers.

Contact of the composition comprising tarnish inhibitor with the plated metal surfaces will be for at least 5 seconds,

preferably for at least 20 seconds. Where the tarnish inhibitor is present in the plating solution, the time of contact is generally determined by the duration of the plating step. Generally, the contact time will be from 1 to 5 minutes. The temperature of contact is most usually from 10 to 90° C., preferably 15 to 75° C., more preferably 20 to 60° C. For example the temperature of contact with the plating solution may be from 15 to 50° C., most usually from 20 to 40° C. Contact may be any conventional means, for example by dip, spray or horizontal immersion coating.

The most appropriate pH depends to some extent on the particular tarnish inhibitor used but primarily on the metal ions present in a plating bath which contains the tarnish inhibitor. Where the tarnish inhibitor is contacted in a separate step with the plated metal surface, the pH should be appropriate for the tarnish inhibitor and selected so that it does not attack the plating. Where the solution is a silver plating composition, a convenient pH is in the range of 3 to 10. Where the solution is a bismuth plating composition, the pH may be 1 or lower.

The solution comprising the tarnish inhibitor may be a final rinse solution, applied to the boards prior to drying of the boards. The board may undergo subsequent treatment steps after contact with the composition comprising tarnish inhibitor. However, generally, after contact with the solution, comprising a tarnish inhibitor and drying, they are at the end of the first bare board manufacturing stage, and are ready for the second component-attachment stages. Optionally, for example, there may be a deionized water rinse step, prior to drying.

The concentration of tarnish inhibitor in the solution comprising tarnish inhibitor will generally be from 0.0001 to 5% by weight, i.e., 0.001 to 50 g/l. Preferably, the amount of tarnish inhibitor will be from 0.005 to 3% by weight, and most preferably from 0.01 to 2% by weight, or even below 1% by weight.

The method of the second aspect of the invention may surprisingly also be used on precious metals such as gold, platinum or ruthenium where it will improve solderability.

In the second aspect of the invention, the metal plating step is preferably an immersion/displacement plating or electroless plating step. It consists of a single step using a single plating composition. Most preferably the plating step will be an immersion/displacement plating step comprising contacting the metal of the pads and/or through-holes with an immersion plating composition.

Where the plating is other than by the preferred immersion/displacement process, for example, if it is by electroless plating, the plating composition may comprise alternative plating metal ions, such as nickel.

The use of tarnish inhibitor in the invention has been found to provide metal coatings which have good tarnish resistance (resistance to humidity and oxidation) even when stored at 40° C. and 93% RH for 96 hours or at 150° C. for 2 hours. The porosity inherent in immersion coatings is reduced by the provision of a level surface using the bright-etch step and using, so that the anti-tarnish properties are considerably improved, even at the high temperatures reached in reflow soldering processes. Concern over the use of silver plating as described for example in DE-C-4316679 due to migration of silver ions is overcome as it has been found that the present invention substantially prevents silver migration by providing a barrier to moisture.

In both the above aspects of the invention, an immersion plating composition preferably contains a complexing agent for the ions of the more electropositive metal.

In a further aspect of the present invention there is provided a displacement metal plating process in which a relatively less electropositive base metal is plated with a relatively more electropositive coating metal by contact with an aqueous plating composition containing ions of the more electropositive metal, a complexing agent for such ions and a tarnish inhibitor for the more electropositive metal so as to form a coating of the more electropositive metal.

In this aspect of the invention there is also provided a new plating composition containing ions of a metal which can be displacement plated, a complexing agent for the ions, preferably present in higher than equimolar amounts as compared to the metal ion, and containing a tarnish inhibitor for the metal, and being substantially free of reducing agent capable of reducing the ion to the metal.

This aspect of the invention has been found to be particularly useful for silver or bismuth plating. Therefore preferably, the plating composition described contains silver or bismuth ions.

The plating composition used in this aspect of the invention may be an immersion plating composition based on any plating composition used in the PCB industry.

In this embodiment of the invention, preferably, prior to contacting the metal surface with the plating composition in the plating step, the metal surface is cleaned. Cleaning may be accomplished using an acidic cleaning composition, such as any cleaning composition known in the art. Examples are copper conditioner PC 1144 supplied by Alpha Metals Limited.

Where there is a cleaning step using an acidic cleaning solution, generally there will be a rinsing step prior to contacting the metal surface with the plating solution.

Preferably any pre-cleaning will include a bright-etch step.

The plating composition may also comprise a complexing agent. If so, the complexing agent is preferably present in an amount of from 0.1 to 250 g/l, preferably from 2 to 200 g/l and most preferably from 10 to 100 g/l, especially around 50 g/l. The complexing agent may be any complexing agent for the plating metal ions which does not form a water insoluble precipitate under the aqueous and pH conditions of the composition. Mixtures of complexing agents may also be used. It is desirable to use complexing agents which are bi-dentate or higher dentate ligands since the stability constants of such complexes are higher than mono-dentate ligands.

Examples of suitable complexing agents have oxygen-containing ligands, for instance amino acids and their salts, preferably having at least 2 and up to 10 carbon atoms, polycarboxylic acids, usually amino acetic acids, such as nitrilo-triacetic acid or, usually, alkylene polyamine poly-acetic acids including ethylene diamine tetra-acetic acid (EDTA), diethylene triamine penta-acetic acid, N-hydroxyethyl ethylene diamine triacetic acid, 1,3-diamino-2-propanol-N,N,N',N'-tetra-acetic acid, bishydroxyphenylethylene diamine diacetic acid, diamino cyclohexane tetra-acetic acid or ethylene glycol-bis-[(β -aminoethylether)-N,N'-tetra-acetic acid] and N,N,N',N'-tetrakis-(2-hydroxypropyl) ethylene diamine, citrates and/or tartrates, N,N-di-(hydroxyethyl)glycine, gluconates, lactates, citrates, tartrates, crown ethers and/or cryptands.

Particularly preferred complexing agents for silver are EDTA, DTPA and N,N,N',N'-tetrakis-(2-hydroxypropyl) ethylene diamine. The complexing agent should form a soluble complex with plating metal ions in aqueous solution under the pH conditions of the plating solution.

A suitable complexing agent for bismuth is chloride, and it is generally unnecessary to use a multidentate (i.e., bi- or higher dentate) ligand complexing agent for bismuth.

The complexing agent is preferably used either in stoichiometric equivalent amounts or in a stoichiometric excess so that all the plating metal ions may be complexed. By stoichiometric we mean equimolar. Preferably the complexing agent is present in a higher molar concentration than the silver ions, the molar ratio preferably being (at least 1.2):1, more preferably (at least 2.0):1, more preferably (at least 3):1.

Suitable tarnish inhibitors for use in all aspects of the present invention include for example:

- (a) fatty acid amines, preferably having at least 6 carbon atoms, most preferably at least 10 carbon atoms and generally no greater than 30 carbon atoms, they may be primary, secondary, tertiary, diamines, amine salts, amides, ethoxylated amines, ethoxylated diamines, quaternary ammonium salts, quaternary diammonium salts, ethoxylated quaternary ammonium salts, ethoxylated amides and amine oxides. Examples of the primary, secondary and tertiary amine-type corrosion inhibitors are ARMEENTM to (TM denotes trademark). Examples of the subsequent amine-type corrosion inhibitors are respectively DUOMEENTM, ARMACTM/DUOMAC, ARMIDTM, ETHOMEENTM, ETHODUONEENTM, ARQUADTM, DUOQUADTM, ETHOQUADTM, ETHOMIDTM, AROMOXTM, all supplied by Akzo Chemie.
- (b) purines and substituted purines.
- (c) N-acyl derivatives of sarcosine, such as the SARKO-SYrange of products supplied by Ciba-Geigy.
- (d) organic polycarboxylic acids such as Reocor 190 supplied by Ciba-Geigy.
- (e) substituted imidazoline in which substituents are for example hydroxyl C₁₋₄ alkyl amino or carbonyl-containing groups. Examples include AMINE 0, produced by Ciba-Geigy, especially in combination with a N-acyl sarcosine of category (c).
- (f) alkyl or alkyl benzyl imidazoles, e.g. undecyl imidazole in which the alkyl group has up to 22 carbon atoms, preferably no greater than 11 carbon atoms and in which the alkyl or benzyl groups are optionally substituted.
- (g) benzimidazoles, especially alkylaryl benzimidazoles in which the alkyl group has up to 22 carbon atoms, preferably no greater than 10 carbon atoms and in which the alkyl or benzyl groups are optionally substituted, for example 2-(p-chlorobenzyl) benzimidazole which is particularly preferred.
- (h) phosphate esters such as EKCOL PS-413, supplied by Witco
- (i) optionally substituted triazole derivatives such as REOMET 42, supplied by Ciba-Geigy. Examples are benzo triazole, tolyl triazole and alkyl substituted triazole derivatives having a carbon number on the alkyl group of from 1 to 22, preferably from 1 to 10.
- (j) substituted tetrazoles, such as 5(3(trifluoromethyl phenyl)) tetrazole, is also a preferred example.

The choice of tarnish inhibitor will depend to some extent upon the metal of the plated metal surfaces, but this will be clear to a person skilled in the art. For example, if the tarnish inhibitor is to be incorporated into a gold plating bath, the tarnish inhibitor may be a chloride salt, however, in contrast, using a silver plating bath, chloride salts may not be used as they will result in formation of an insoluble silver chloride precipitate.

The tarnish inhibitor is preferably water soluble so that the solution is an aqueous solution. However, water immiscible tarnish inhibitors may be used although it may be necessary to include a surfactant/cosolvent in the solution.

This invention has been found to provide considerable advantages in preventing tarnishing and conferring humidity resistance on the bare boards produced so that additional protection is provided between the bare board manufacture stage and the component-attachment stage. Solderability is found to be enhanced.

A suitable pH for a silver plating composition may be from 2 to 12, but is preferably from 4 to 10. Thus, the composition may be acidic, up to pH 7. Alternatively, the composition may be alkaline, and have a pH of greater than 7, or even greater than 7.5. A bismuth plating solution usually has a low pH of 1 or less.

A buffering agent may be included in the plating composition to ensure that the pH of the composition is within the desired range. As the buffering agent, any compatible acid or base may be included. A compatible acid or base is an acid or base which in the amounts required in the composition does not result in the precipitation out of solution of the silver ions and/or complexing agent. For example hydrogen chloride is unsuitable for a silver plating composition as it forms an insoluble silver chloride precipitate. Suitable examples include sodium or potassium hydroxide or a carbonate salt, or where acids are required, suitable acids may include citric acid, nitric acid or acetic acid. Borates, phthalates, acetates, phosphonates may be used but the buffer should not result in precipitation of the metal salts and preferably does not inhibit the plating rate. An appropriate buffer will be dependent on the desired working pH.

The plating composition may include optional ingredients such as surfactants or wetting agents to improve the coating uniformity. Where surfactants are included, preferably they are introduced into the composition in an amount such that in the plating bath, they will be present at a concentration of from 0.02 to 100 g/l. Preferably they will be incorporated at a concentration of from 0.1 to 25 g/l and most preferably at a concentration of from 1 to 15 g/l. Any standard surfactant or wetting agent useful in a plating bath may be used. Nonionic surfactants are preferred. Particularly preferred surfactants are alkyl phenol ethoxylates, alcohol ethoxylates and phenol ethoxylates such as *Synperonic NP9 (ex. ICI), *Synperonic A14 (ex. ICI) and *Ethylan HB4 (ex. Harcros), respectively (*denotes trade name).

A further optional ingredient which can be included in the plating baths of the present invention are grain refiners. Grain refiners improve the appearance of the plated metal surfaces by causing formation of smaller crystals of plated metal having a more densely packed structure. Suitable examples of grain refiners include lower alcohols such as those having from 1 to 6 carbon atoms, for example isopropanol and polyethylene glycols, for example PEG 1450 (Carbowax* Union Carbide). Grain refiners may be incorporated in the composition in amounts from 0.02 to 200 g/l. More preferably, if a grain refiner is included, it will be at concentrations of from 0.05 to 100 g/l and most preferably from 0.1 to 10 g/l. Any nonaqueous solvent should be present in amounts below 50% by weight of the composition, preferably below 30% by weight or even below 10% or 5% by weight of the plating composition.

Other non-active, non-interfering components may be included such as defoamers especially for spray applications (e.g., A100 supplied by Dow), dyes, etc.

The balance in the composition is water. Deionized water or other purified water which has had interfering ions

removed, is used in the plating composition used in the process of the invention.

In order to form the plating composition for use in the processes of the present invention, preferably a solution is firstly prepared comprising deionized water, complexing agent as defined above, and any buffering agent, optionally with the other optional ingredients, and a salt of the more electropositive metal is added as an aqueous solution to the other components which have been formed into a pre-mix. It has been found that this is the most advantageous way to prepare the solution because trying to dissolve the metal salt directly into the plating composition is relatively time consuming and, where the metal is silver, tends to be more vulnerable to photo-reaction which results in precipitation of silver ions out of solution, as a dark precipitate.

Preferably the pH of the composition to which a silver salt is added will be from pH 3 to 10, most preferably from 4 to 8.

The components are mixed until they have substantially dissolved. The use of heat for silver dissolution is disadvantageous because again, it may tend to cause the formation of a dark silver precipitate.

After contact of the bare board with the solution comprising tarnish inhibitor, the board is dried. Preferably, there will be no post-rinse step between contact of the board with the solution and drying.

Drying may be by any means, but is generally using warm air, for example treated metal may be passed through a drying oven.

The coating obtained using the method of the present invention produces a surface which is considerably more uniform and even than that obtained in the conventional HAL processes and, compared with organic protection, the coating is more resistant to soldering operations. Furthermore, the process of this invention is less expensive and simpler than use of the nickel/gold process.

In the subsequent component-attachment stage, the components are soldered onto the plated pads and/or through-holes of the bare board. The metal of the pad(s) and/or through-holes (generally copper) and plating metal, usually silver, and/or the plating metal and solder may tend to intermix. The bond formed with the components has good electrical conductivity and good bond strength.

After component attachment, finished boards having components attached over the plated layer of the present invention, do not suffer joint reliability problems as do those boards formed using a nickel/gold step.

EXAMPLE 1

A composition was prepared in which 50 g EDTA and 20.4 g of solid sodium hydroxide were mixed with sufficient water to dissolve them. A solution comprising 1 g silver nitrate in deionized water was subsequently added to the premixture comprising EDTA and sodium hydroxide solution and deionized water was added to 1 liter. Copper double-sided circuit boards, having a variety of surface mount feature and plated through-holes of various diameter were coated with the silver solution using the following procedure.

Boards were chemically brightened in an aqueous solution of 20% v/v H_2O_2 (35%), 0.5% v/v H_2SO_4 (96%), 2.5% 1,4-butanediol for 1 minute. A tap water rinse was then employed, followed by an acid rinse in 10% H_2SO_4 for 1 minute. The boards were given a further water rinse, then immersed in the silver plating solution at 40° C. for 4 minutes. After removal from the bath, the boards were rinsed with water and warm air dried. Copper areas of the board were coated with a bright, even silver deposit.

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Coated boards were subjected to three passes through a typical IR silver paste reflow profile (see FIG. 1), then wave soldered using NR300, an Alpha Metals VOC free, no clean flux. 100% filing of the plated through-holes with solder was achieved.

Further boards were stored in a humidity cabinet at 40° C./93% RH for 24 hours before being passed through 3 IR reflow profiles. These boards showed a slight degree of tarnishing on the silver coating. However 100% hole filling was still achieved during subsequent wave soldering with NR 300 flux.

EXAMPLE 2

A silver plating solution was prepared by forming a solution comprising 50 g EDTA, 20.4 g NaOH, 14 g Ethylan HB4 (Akros Chemicals), 3 g Crodamet 02 (Croda Chemicals) in 800 mls deionized water. To this solution was added a solution of 1 g AgNO₃ in 100 mls deionized water. The pH was adjusted to 6.8 by addition of dilute NaOH/HNO₃, then made up to 1 liter with deionized water.

Double sided bare copper boards were coated with the above solution using the procedure as described in Example 1. 100% filling of plated through-holes with solder was achieved during wave soldering with NR300 flux after passage through 3 IR reflow profiles.

Boards stored at 40° C./93% RH for 24 hours prior to passage through 3 IR reflow profiles showed no evidence of tarnishing and soldered well during wave soldering trials, giving 100% hole filling.

EXAMPLE 3

Double-sided bare copper boards were coated using the bath composition and procedure as described in Example 1. Following removal of the boards from the silver plating solution and rinsing, the boards were immersed in a solution of 4 g Reomet 42 (Ciba-Geigy) in 1 liter deionized water (pH 7) for 1 minute at room temperature. The boards were then rinsed in tap water and warm air dried. A bright even silver coating was produced.

The coated boards were stored at 4° C./93% RH for 24 hours then passed through 3 IR paste reflow profiles. The boards showed no evidence of tarnishing, and soldered well when wave soldered using KR 300 flux.

EXAMPLE 4

Coupons of copper strip (5 cm×1 cm) were coated with the silver coating as described in Example 2. In addition, further samples were coated with immersion tin, 63/37 Sn/Pb and two competitors solderability preservative coatings based on substituted benzimidazole chemistry. The following coating procedures were applied for the various samples:

Immersion Tin Coating

Coupons were etched in an aqueous solution of Na₂S₂O₈ (5%), H₂SO₄ (5%) for 2 minutes, rinsed with tap water, then rinsed with 10% H₂SO₄, for 1 minute and then rinsed with deionized water. The coupons were then immersed in an immersion tin plating solution comprising 0.33 g/l Sn(BF₄)₂ 150 g/l thiourea, 20 g/l fluoroboric acid and 5 g/l Synparonic NP9 (ex. ICI) in deionized water, for 1 minute at room temperature. The coupons were then rinsed with deionized water and warm air dried.

Sn/Pb Coating

Coupons were etched in an aqueous solution comprising Na₂S₂O₈, (5%) and H₂SO₄ (5%), rinsed with tap water then

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with 10% H₂SO₄ and then with deionized water. The coupons were warm air dried. Alpha NR 300 flux was then applied to each coupon. The coupons were then coated 63/37 Sn/Pb by immersion in molten solder at 250° C. for 3 seconds.

Azole 1 and Azole 2

Coupons were etched and rinsed as for the immersion tin samples. Coupons were then immersed in the solution containing the azole at 40° C. for 90 seconds. After removal from the azole containing solution, the coupons were rinsed with deionized water, and warm air dried.

The coupons were subjected to a variety of different pretreatments.

A.	No pre-treatment.
B.	Passage through 3 solder paste reflow profiles.
C.	Storage at 40° C./93% RH for 96 hours.
D.	Storage at 40° C./94% RH for 96 hours, then 3 solder paste reflow profiles.
E.	Storage at 150° C. for 2 hours.

Samples were then soldered using a meniscograph with NR300 flux.

The meniscograph test method monitors the solderability by measuring the net force acting between specimen and solder. The coatings are assessed by the length of time to reach zero wetting force, and the size of the equilibrium wetting force. To achieve good results in wave soldering a short wetting time and high equilibrium wetting force are preferred.

The table below shows the wetting times in seconds and wetting forces after 2 seconds immersion in mN/mm for various copper coated samples.

As can be seen from above, the silver coatings prepared according to this invention have shorter wetting times and higher wetting forces than the Sn and benzimidazole alternative and retain these properties more readily after humidity and heat treatment.

TABLE 1

Coating	Pre-Treatment	Wet Time/Sec	Wetting Force at 2 Seconds
Example 2	A	0.7	0.429
Example 2	B	0.8	0.444
Example 2	C	0.7	0.429
Example 2	D	0.7	0.441
Example 2	E	0.8	0.438
Tin	A	0.9	0.488
Tin	B	>5	-0.028
Tin	C	>5	0.008
Tin	D	>5	-0.148
Azole 1	A	0.8	0.439
Azole 1	B	0.9	0.412
Azole 1	C	0.9	0.443
Azole 1	D	0.9	0.426
Azole 1	E	1.0	0.421
Azole 2	A	0.9	0.449
Azole 2	B	1.0	0.417
Azole 2	C	0.9	0.466
Azole 2	D	1.1	0.310
Azole 2	E	1.2	0.296
Sn/Pb	A	0.8	0.475
Sn/Pb	B	0.8	0.501
Sn/Pb	C	0.8	0.492
Sn/Pb	D	0.8	0.474
Sn/Pb	E	0.8	0.492

EXAMPLE 5

A displacement bismuth plating composition was prepared comprising 3.9 g bismuth oxide, 183.1g hydrogen

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chloride (as 37% solution), 490.Sg glycolic acid (70% solution), 265.4 g (50% sodium hydroxide solution), 0.077 g potassium iodide, 0.003 g Synperonic NP9 (ex. ICI) and 4 g 2p-chlorobenzyl benzimidazole, were added to de-ionized water to make 1 liter of product solution Bare boards having copper pads and copper through-holes were chemically brightened as described in Example 1, then immersed in the plating baths for 2 minutes at 70° C. A coating of bismuth was formed on the surface of the copper having a thickness of 0.05 μ m. Subsequent solderability and tarnish resistance tests carried out on the plated bare boards showed good results for solderability and tarnish resistance.

EXAMPLE 6

Double-sided bare copper boards were bright etched in an aqueous solution of 50% v/v HNO₃, 10% H₂SO₄, 10% H₃PO₄, 1% HCl for 1 minute at room temperature. Boards were then rinsed in tap water followed by 10% H₂SO₄ for 1 minute. After a further water rinse, boards were immersed in silver plating bath described in Example 2 for 4 minutes at 45° C. Boards were then water rinsed and warm air dried.

The coated boards were stored at 40° C./93% RH for 24 hours then passed through 3 IR paste reflow profiles. The boards showed no evidence of tarnishing when wave soldered using NR 300 flux.

EXAMPLE 7

A silver plating bath was prepared by forming a solution comprising 64.8 g diethylene triamine penta-acetic acid, 23.0 g NaOH, 24 g surfactant Ethylan HB4 (Akros Chemicals), 2.5 g Crodamet 02 an ethoxylated 3° amine compound (Croda Chemicals) in 800 mls deionized water. To this solution was added a solution of 1 g silver nitrate in 100 mls deionized water. The pH of this solution was adjusted to 6.9 by addition of dilute NaOH solution or nitric acid. The volume was then made up to 1 liter using deionized water.

Double-sided bare copper boards were coated using the above solution using the procedure as described in Example 1. 100% filling of the plated through-holes was achieved during wave-soldering of the coated boards using Alpha Metals MR300 flux after passage through 3 IR reflow profiles showed no evidence of tarnishing, and soldered well during wave-soldering trials giving 100% hole-fill.

EXAMPLE 8

An immersion silver plating solution was prepared comprising 98.2 g deionized water, 1 g of nitric acid, 0.1 g of silver nitrate, 0.3 g of Chemeen C2 (antitarnish) and 0.4 g Mazawet DF (solubilizer). The pH was adjusted to 6 using a 50% solution of ethylene diamine. The bath produced an adherent silver deposit on copper coupons which showed good solderability and humidity resistance.

EXAMPLE 9

A bismuth plating solution was prepared containing bismuth trioxide 2.1% weight, hydrochloric acid (22° Be) 46.73% weight, glycolic acid (70%) 49.5% weight, potassium chloride 0.07% weight, polyethylene glycol 600 0.1% weight, Chemax Chemeen C2 0.2% weight, distilled water 1.2% weight and tartaric acid 0.1% weight. A further solution was prepared from which the Chemeen C2 was omitted. Samples of copper clad printed circuit material were plated in each of the solutions. These plated samples were then placed in a humidity chamber for 16 hours at 60° C. and 95% relative humidity.

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After this exposure the samples were examined, and those prepared in the solution without the Chemeen C2 were heavily tarnished. The samples prepared in the solution containing the tarnish inhibitor had a good appearance with minimal oxidation, and when tested showed good solderability.

Other embodiments of the invention are to be considered within the scope of the appended claims.

What is claimed is:

1. A plating solution comprising:

a solvent;

metallic ions dissolved in the solvent; and

a tarnish inhibitor in the solvent, the tarnish inhibitor characterized in that it does not cause the dissolved metallic ions to precipitate in the solution.

2. The plating solution of claim 1, wherein the metallic ions are selected from the group consisting of nickel, silver, tin, lead, palladium, cobalt, gold, platinum, bismuth and combinations thereof.

3. The plating solution of claim 2, wherein the metallic ions include silver ions.

4. The plating solution of claim 1, wherein the solvent comprises water.

5. The plating solution of claim 1, wherein the tarnish inhibitor is present at a concentration in the range from 0.001 to 50 g/l.

6. The plating solution of claim 5, wherein the tarnish inhibitor is present at a concentration in the range from 0.05 to 30 g/l.

7. The plating solution of claim 6, wherein the tarnish inhibitor is present at a concentration in the range from 0.1 to 20 g/l.

8. The plating solution of claim 7, wherein the tarnish inhibitor is present at a concentration of less than 10 g/l.

9. The plating solution of claim 1, further comprising a complexing agent for the dissolved metallic ions.

10. The plating solution of claim 9, wherein the complexing agent includes a multidentate ligand.

11. The plating solution of claim 10, wherein the complexing agent includes an oxygen-containing ligand.

12. The plating solution of claim 1, wherein the complexing agent is present at a concentration that is the stoichiometric equivalent or greater than the concentration of the dissolved metallic ions.

13. The plating solution of claim 1, wherein the complexing agent is present at a concentration of 0.1 to 250 g/l.

14. The plating solution of claim 13, wherein the complexing agent is present at a concentration of 2 to 200 g/l.

15. The plating solution of claim 14, wherein the complexing agent is present at a concentration of 10 to 100 g/l.

16. The plating solution of claim 15, wherein the complexing agent is present at a concentration of about 50 g/l.

17. The plating solution of claim 1, wherein the plating solution has a pH in the range from 2 to 12.

18. The plating solution of claim 17, wherein the plating solution has a pH in the range from 4 to 10.

19. The plating solution of claim 18, wherein the plating solution has a pH of about 7.

20. A silver-plating solution comprising:

water;

a source of silver ions dissolved in the water; and

a tarnish inhibitor in the water at a concentration from 0.0001 to 5% by weight of the silver-plating solution, the tarnish inhibitor characterized in that it does not cause the dissolved silver ions to precipitate in the solution.

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21. The silver-plating solution of claim 20, wherein the tarnish inhibitor is at a concentration in the range from 0.005 to 3% by weight.

22. The silver-plating solution of claim 20, wherein the tarnish inhibitor is at a concentration in the range from 0.01 to 2% by weight. 5

23. The silver-plating solution of claim 20, wherein the plating solution has a pH in the range from 4 to 10.

24. The silver-plating solution of claim 23, further comprising a complexing agent for the silver ions. 10

25. The silver-plating solution of claim 24, wherein the complexing agent is a multidentate ligand.

26. The silver-plating solution of claim 25, wherein the complexing agent is present at a concentration that is the stoichiometric equivalent or greater than the concentration of the dissolved metallic ions. 15

27. The silver-plating solution of claim 26, wherein the complexing agent is present at a concentration of 0.1 to 250 g/l.

28. An aqueous plating composition suitable for forming an immersion plating of a first metal having a first electropositivity on a substrate formed of a second metal having a 20

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second electropositivity, the first electropositivity being greater than the second electropositivity, the composition comprising:

ions of the first metal;

a complexing agent for the ions of the first metal; and

a tarnish inhibitor for the first metal, the composition being substantially free of any reducing agent for the ions of the first metal.

29. A composition according to claim 28, wherein the tarnish inhibitor composes from 0.001 to 5% by weight of the composition.

30. A composition according to claim 28, wherein the ions of the first metal are selected from the group consisting of nickel ions, silver ions, tin ions, lead ions, palladium ions, cobalt ions, gold ions, platinum ions, bismuth ions and mixtures thereof.

31. A composition according to claim 30, wherein the ions of the first metal are silver ions.

* * * * *

United States Patent [19]

Nelson et al.

[11] Patent Number: 4,846,918

[45] Date of Patent: Jul. 11, 1989

[54] COPPER ETCHING PROCESS AND
PRODUCT WITH CONTROLLED NITROUS
ACID REACTION

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A. Martens, Fremont, both of Calif.

[73] Assignee: Psi Star, Fremont, Calif.

[21] Appl. No.: 159,727

[22] Filed: Feb. 24, 1988

[51] Int. Cl.⁴ C23F 1/00

[52] U.S. Cl. 156/628; 156/666;
156/901

[58] Field of Search 134/3; 156/628, 635,
156/656, 666, 901, 902

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Primary Examiner—David L. Lacey

Assistant Examiner—L. Johnson

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Albritton & Herbert

[57] ABSTRACT

Copper etching process and product in which a material which promotes the formation of nitrous acid is included in the copper. The copper is etched in a nitric acid solution, and the nitrous acid catalyzes the reaction between the nitric acid and the copper. The catalyst promoter is distributed within the copper to control where the nitrous acid is formed and, hence, the manner in which the copper is etched. In one disclosed embodiment, the material which promotes the formation of nitrous acid increases in concentration toward the substrate, or board to which the copper is bonded. The nitrous acid reacts vigorously with the copper, and the etch rate increases as the etch progresses through the copper toward the substrate. A polymer and/or a nitrous acid scavenger can be included in the etching solution to confine the etching reaction to the region in which the nitrous acid is formed.

14 Claims, No Drawings

COPPER ETCHING PROCESS AND PRODUCT WITH CONTROLLED NITROUS ACID REACTION

This invention pertains generally to the etching of copper, and more particularly to a process and product which are particularly suitable for use in the manufacture of printed circuit boards.

In the manufacture of printed circuit boards, a conductive layer of copper is laminated to an insulative substrate such as a fiberglass-epoxy board, and portions of the copper are etched away to leave the desired circuit patterns. The areas to be left are generally defined by a mask of etch resistant material which is applied to the board prior to etching, then stripped away upon completion of the etching process.

One problem commonly encountered in the etching process is the tendency of the copper to etch laterally under the resist material at the same time that it is being removed vertically. The ratio of vertical etching to lateral etching is commonly referred to as the etch ratio. If the etch ratio is 1:1, the etch is said to be isotropic, and if it is greater than 1:1, the etch is said to be anisotropic.

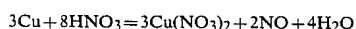
U.S. Pat. No. 4,497,687 describes an improved process for anisotropically etching copper foil in the manufacture of printed circuit boards. This process utilizes an aqueous solution of nitric acid as an etchant, and it overcomes many of the problems of the other etching processes of the prior art. U.S. Pat. No. 4,545,850 discloses a somewhat similar process in which the etching solution is regenerated by adding sulfuric acid. Even with these improved processes, some instances have been encountered in which there has been inexplicable lateral etching or undercutting of the copper.

It is in general an object of the invention to provide a new and improved copper etching process and product in which lateral etching or undercutting is reduced substantially.

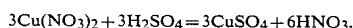
Another object of the invention is to provide an etching process and product of the above character in which anisotropic etching is achieved consistently.

These and other objects are achieved in accordance with the invention by etching the copper in a nitric acid solution and by including in the copper a material which promotes the formation of nitrous acid which catalyzes a reaction between the nitric acid and the copper to dissolve the copper. The catalyst precursor material is distributed within the copper to control the removal of the copper, and in one disclosed embodiment it increases in concentration toward the substrate, or board, to which the copper is bonded so that the etch rate increases as the etch progresses through the copper toward the substrate. A polymer and/or a nitrous acid scavenger can be included in the etching solution to confine the etching reaction to the region in which the nitrous acid is formed.

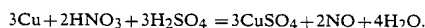
In the nitric acid etching chemistry disclosed in U.S. Pat. Nos. 4,497,687 and 4,545,850, nitric acid reacts with copper according to the relationship



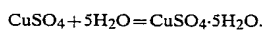
with the nitric acid serving both as an oxidant and as an anion source for the dissolved copper. The dissolved copper is removed by adding sulfuric acid to precipitate the copper according to the relationship



To protect the etch resist and the substrate board from attack by the nitric acid, either copper nitrate or sulfuric acid is included in the etching solution. When sulfuric acid is employed, the consumption of nitric acid is reduced, and the reaction proceeds according to the relationship



Copper is removed as the sulfate pentahydrate according to the relationship



The copper nitrate or sulfuric acid increases the reactivity of nitric acid toward copper such that reasonable reaction rates can be achieved with much lower concentrations of nitric acid than would otherwise be required. Thus, the amount of nitric acid can be kept to levels which do not react with the substrates or organic resists. Certain metal resists can also be utilized with these etchants, including tin, nickel and alloys thereof.

A polymer is included in the etching solution to control the surface reaction rate and to enhance the anisotropy of the etch. One suitable polymer is a polyacrylamide which is soluble in water and has a high molecular weight. The amount of polymer employed is on the order of 0.05% (volume) of the solution. Suitable polyacrylamides include Hercules Reten 520 (a neutral polyacrylamide having a high molecular weight), and American Cyanamid's Magnifloc 2535 CH polyacrylamide.

A surfactant can also be included in the etching solution to reduce surface tension and facilitate the movement of nitric oxide bubbles from the surface of the copper. The nitric oxide gas is generated during the etching process, and the surfactants serve to keep the bubble size small and prevent the bubbles from bridging between resist lines and blocking etching between the lines. Only a very small amount of surfactant is required, e.g. 0.1 to 0.2% (volume) of the etching solution. Suitable surfactants include fluorocarbon surfactants such as 3M's FC-100 (an amphoteric surfactant) and FC-135 (a cationic surfactant). In some processes such as spray etching, the surfactant may not be necessary and can even impede the etching process.

The reaction between copper and nitric acid is catalyzed by nitrous acid. Even though copper will not react with pure nitric acid at any concentration, once even a small amount of nitrous acid is introduced, a vigorous reaction commences between the nitric acid and the copper. One of the products of this reaction is more nitrous acid, and once initiated, the reaction tends to support itself, accelerating as it does so. Thus, the reaction between copper and nitric acid is autocatalytic with respect to nitrous acid.

It has now been found that the character of the etch can be controlled and anisotropy can be improved substantially by including in the copper a material which promotes the formation of nitrous acid and by including a polymer and/or a nitrous acid scavenger in the etching solution to control the nitrous acid which is formed.

Since nitric acid itself does not react with copper, and the use of a nitric acid solution depends upon the presence of the catalyst nitrous acid to dissolve the copper, by controlling where the nitrous acid is formed and where it is available for interaction with the copper, it is possible to control the manner in which the copper is removed.

For anisotropic etching on a printed circuit board, the material which promotes the formation of nitrous acid is distributed nonuniformly within the copper with a gradient such that the material has a relatively high concentration near the substrate, or board, and a relatively low concentration toward the outer surface of the copper. The concentration gradient can be formed, for example, in a copper layer formed by electroplating by decreasing the ratio of the catalyst promoter material to the copper as the plating progresses. It can also be formed by depositing the catalyst promoter material on a surface of the copper and diffusing it into the copper, or by any other suitable technique.

Suitable catalyst promoter materials include copper alloying metals such as zinc, tin, cadmium, magnesium, aluminum, the alkali metals (lithium, sodium, potassium, rubidium and cesium) and, to some extent, iron and lead. These metals do not require the presence of nitrous acid to react with nitric acid, and upon such reaction they either produce nitrous acid directly or a precursor to nitrous acid.

A polymer having a high molecular weight and an affinity for copper can be added to the etching solution to minimize diffusion of nitrous acid from the bottom surface of the etched region toward the top of the sidewall. Polyacrylamide and derivatives of it have been found to be suitable for this purpose. The polymer forms a thin adsorption layer on the copper during the etching process. This layer inhibits diffusion of the nitrous acid along the surface of the copper, but has relatively little effect on the exchange of reactants and products between the copper and the bulk of the etchant. Thus, nitrous acid generated in a particular region is likely to react with copper in the same region or diffuse into the bulk of the etchant and be diluted. It is less likely to diffuse along the copper surface and react with copper in a distant region.

A nitrous acid scavenger can be added to the etching solution to deplete the nitrous acid away from the interface between the solution and the copper. By controlling the concentration of the nitrous acid in this manner, the etching reaction is controlled, and copper is removed only at the interface where the catalyst promoter is present and the nitrous acid is generated. Suitable scavengers include urea, hydrogen peroxide, hydrazine, sulfamic acid, and combinations thereof.

It has been found that one particularly satisfactory and commercially available source of copper for use in the invention is a 9 micron copper foil grown on an aluminum carrier foil by Gould, Inc. Prior to deposition of the copper, the aluminum is given a zincating treatment, which serves to overcome a chemical incompatibility which prevents the copper from being electrodeposited directly on the aluminum. Although the zinc coating is substantially removed, enough of the zinc remains to be effective as an interface for copper deposition. After the copper has been deposited, a thin layer of electroplated zinc is formed on the exposed surface to the copper to protect it. The thickness of the electroplated layer is much greater than the zinc which remains at the interface between the copper and the aluminum.

The copper foil thus formed is then laminated to a standard epoxy-fiberglass substrate, and the aluminum foil is removed from the outer surface of the copper. The temperature and pressure conditions employed in the lamination process cause the copper and zinc to alloy and form a brass. Some of zinc layer diffuses into

the copper foil, giving the foil a zinc gradient which decreases in concentration from the substrate toward the outer surface of the copper. The relatively small amount of zinc remaining from the first zincating step has a negligible effect on the zinc gradient.

Another 9 micron copper foil grown on an aluminum carrier is available commercially from Metallverken Foils AB, Perstorp, Sweden. This foil is similar to the Gould 9 micron foil in that the copper is grown on an aluminum carrier foil with a zincate layer on the aluminum. It differs from the Gould foil in that the zincate layer is not removed before the copper is deposited, and the exposed surface of the copper foil is protected by a chromate deposit rather than zinc. When this foil is laminated to a substrate board, any alloying of copper and zinc occurs at the aluminum-copper interface, not at the copper-substrate interface. The gradient produced by diffusion of the zinc into the copper is reversed, and the higher zinc concentration is at the outer surface of the copper, not toward the substrate. When this board is etched in a nitric acid solution, the etch is isotropic.

A board with the Metallverken foil can be etched anisotropically by forming a thin layer of a suitable material such as zinc on the substrate side of the copper foil before it is laminated to the substrate. The zinc from this layer will diffuse into the copper as it does in the Gould foil, producing the desired gradient.

When a board having either the Gould foil or the Metallverken foil with a layer of zinc on the substrate side of the copper is etched in a nitric acid solution, the etch is anisotropic because the etch rate increases as the dissolution of copper proceeds toward the substrate due to the increasing production of nitrous acid initiated by the zinc. The vertical etching reaction is thus catalyzed relative to the lateral reaction due to an increase in the reaction catalyst as a function of the depth of the etch. Enhancement of the anisotropy is observed when a nitrous acid scavenger, such as urea, is added to the etching solution. The scavenger depletes the bulk nitrous acid concentration so that the reaction between the copper and the nitrous acid can occur only in the presence of the zinc which generates the necessary catalytic amounts of nitrous acid at the interface between the etchant and the reacting surface of the copper.

A circuit board manufactured in accordance with the invention has a layer of copper on a substrate such as a fiberglass-epoxy board, with a catalyst precursor material which reacts with nitric acid to form nitrous acid distributed within the copper to control the manner in which the copper is removed by a nitric acid etchant. In one preferred embodiment, the precursor is distributed with a higher concentration toward the substrate than toward the outer surface of the copper so that the etch rate will increase toward the substrate when the board is etched in a nitric acid solution.

This results in an etch which is substantially more anisotropic than it would be without the catalyst precursor gradient.

It is apparent from the foregoing that a new and improved copper etching process and product have been provided for use in the manufacture of printed circuit boards. While only certain presently preferred embodiments have been described in detail, as will be apparent to those familiar with the art, certain changes and improvements can be made without departing from

the scope of the invention as defined by the following claims.

We claim:

1. In a process for manufacturing a printed circuit board in which copper is removed by etching in a nitric acid solution, the steps of: providing a substrate with a layer of copper having a nonuniform distribution of catalyst precursor material within the copper for promoting the formation of nitrous acid from nitric acid in a controlled manner, forming an etch resist mask over the copper with a portion of the copper being exposed through the mask, and contacting the exposed portion of the copper with the nitric acid solution to bring about the formation of nitrous acid and the removal of copper in accordance with the distribution of the catalyst precursor material within the copper.
2. The process of claim 1 wherein the catalyst precursor material decreases in concentration from the substrate toward the outer surface of the copper layer.
3. The process of claim 1 wherein the catalyst precursor material is selected from the group consisting of zinc, tin, cadmium, magnesium, aluminum, and alkali metal, iron, lead, and combinations thereof.
4. The process of claim 1 wherein the nitric acid solution contains a nitrous acid scavenger which depletes the nitrous acid concentration away from the interface between the solution and the copper.
5. The process of claim 4 wherein the nitrous acid scavenger is selected from the group consisting of urea, hydrogen peroxide, hydrazine, sulfamic acid, and combinations thereof.
6. The process of claim 1 wherein the nitric acid solution contains a polymer which forms an adsorption layer on the copper during etching to inhibit diffusion of the nitrous acid along the copper.

7. The process of claim 6 wherein the polymer is selected from the group consisting of polyacrylamide and derivatives thereof.

8. The process of claim 1 wherein the nitric acid solution contains a polymer which has a high molecular weight and an affinity for copper.

9. The process of claim 1 wherein the nitric acid solution is an aqueous solution which contains nitric acid, copper nitrate or sulfuric acid, and a polymer.

10. The process of claim 9 wherein the nitric acid solution also contains a surfactant.

11. The process of claim 1 including the step of adding sulfuric acid to the solution after some of the copper has been dissolved to convert copper nitrate formed by the dissolution of the copper to nitric acid and a copper precipitate.

12. In a process for manufacturing a printed circuit board, the steps of: providing a substrate with a layer of copper on one side thereof, said layer of copper having a nonuniform distribution of catalyst precursor material therein for promoting the formation of nitrous acid from nitric acid in a controlled manner, and exposing the copper to a nitric acid etching solution to bring about the formation of nitrous acid and the removal of copper in accordance with the distribution of the catalyst precursor material within the copper.

13. The process of claim 12 wherein the catalyst precursor material decreases in concentration from the substrate toward the outer surface of the layer of copper.

14. The process of claim 12 wherein the catalyst precursor material is selected from the group consisting of zinc, tin, cadmium, magnesium, aluminum, an alkali metal, iron, lead, and combinations thereof.

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United States Patent [19]**Preisler et al.**[11] **Patent Number:** **5,362,712**[45] **Date of Patent:** **Nov. 8, 1994**[54] **PROCESS FOR REMOVING A COPPER
MOLD FROM A MOLDED BODY**[75] Inventors: **Eberhard Preisler; Joachim Bock,**
both of Erftstadt, Germany[73] Assignee: **Hoechst Aktiengesellschaft,**
Frankfurt am Main[21] Appl. No.: **81,855**[22] Filed: **Jun. 23, 1993****Related U.S. Application Data**

[63] Continuation of Ser. No. 741,248, Aug. 2, 1991, abandoned.

[30] **Foreign Application Priority Data**

Aug. 17, 1990 [DE] Germany 4026015.1

[51] Int. Cl.⁵ **H01L 39/12; C23F 1/00**[52] U.S. Cl. **505/410; 156/656;**
156/666; 264/317; 505/450[58] **Field of Search** 264/317; 505/1, 739,
505/728, 782, 410, 450; 156/625, 628, 656, 666;
252/79.1, 79.2; 423/658.5[56] **References Cited****U.S. PATENT DOCUMENTS**2,414,226 1/1947 Everett 264/317
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0214602 12/1984 Japan 264/317
1016807 1/1986 Japan 264/317*Primary Examiner*—Christopher A. Fiorilla*Attorney, Agent, or Firm*—Connolly and Hutz

[57]

ABSTRACT

In the process for producing molded bodies from precursors of oxidic high-temperature superconductors a copper mold of the desired shape which encloses a solidified bismuth strontium calcium cuprate melt is treated with a solution of a soluble compound containing sulfate anions, an aqueous mineral acid and an oxidizing agent until the copper mold is dissolved. A protective layer of at least one of strontium sulfate or calcium sulfate is formed on the solidified melt.

5 Claims, No Drawings

PROCESS FOR REMOVING A COPPER MOLD FROM A MOLDED BODY

This application is a continuation of application Ser. No. 07/741,248 filed on Aug. 2, 1991, now abandoned.

The melt synthesis of high-temperature superconductor materials based on bismuth strontium calcium cuprate is described in DE 3,830,092 A1. The "BSCCO" high-temperature superconductors which can be prepared according thereto or in another known manner have the composition $\text{Bi}_2(\text{Sr},\text{Ca})_3\text{Cu}_2\text{O}_x$ ("2-layer compound"), the ratio of strontium to calcium being (2 to 5) : 1 (BSCCO stands for bismuth strontium calcium copper oxide). In addition, "1-layer compounds", $\text{Bi}_2(\text{Sr},\text{Ca})_2\text{CuO}_x$, and "3-layer compounds", $\text{Bi}_2(\text{Sr},\text{Ca})_4\text{Cu}_3\text{O}_x$, are known as BSCCO high-temperature superconductors. The oxygen index "x" is set by the sum of the valencies of Bi, Sr, Ca and Cu, but is variable to the extent that Bi may be tri- or pentavalent and Cu may be mono- or divalent.

DE 3,830,092 A1 also mentions the production of molded bodies from the bismuth strontium calcium cuprates. Such molded bodies can be obtained, for example, by casting in variously shaped molds which are preferably composed of copper if the mold is open as, for example, in the case of a cavity having inclined sidewalls or a half cylinder and permits the removal of the casting in terms of shape. It is also important that the casting is carried out with the mold cold so that the solidifying melt cools so rapidly at the mold wall that a chemical reaction with the copper of the mold wall does not occur. Even if the mold wall is flexible and is composed, for example, of a thin metal sheet which can be bent aside after cooling, there are no problems.

Substantially more difficult is the production of more complicated molded bodies which necessitate a substantially closed mold possibly having a complicated shape. In such cases, even the principle of a rapid cooling to avoid the wall reaction cannot always be used because the mold possibly has to be preheated to avoid an unduly premature solidification of the melt flowing in. In comparatively simple cases, for example in the production of fairly thick cylindrical molded bodies by casting in a tubular mold, a mechanical removal of the casing material is still conceivable, for instance by separating the mold wall into two half shells. However, this is no longer an attractive process even for relatively small diameters and can no longer be used in the case of complicated geometries such as rings or coils.

In order to convert a melt of the composition corresponding to the high-temperature superconductor into the superconducting state after solidification, a subsequent heat treatment of the solidified melt of 6 to 30 hours duration at temperatures around 800° C. in air or oxygen is necessary. However, only one metal is known which is suitable as casing material for BSCCO high-temperature superconductors and is permeable to oxygen at the heat treatment temperatures and, consequently, makes possible the conversion of the solidified melt into the desired high-temperature superconductor inside the metal casing: silver. Unfortunately, at 960.8° C., the melting point of silver is below the temperature at which the superconductor melt has to be in order to be capable of being reliably cast. Thus, a silver mold would melt before the superconductor melt had solidified.

For this reason, it is necessary to resort to copper molds since copper is the only system-immanent metal which is suitable for the present purpose. However, a removal of the copper from the solidified melt is absolutely necessary.

Since the mechanical stripping of the copper mold is only of limited practicability, its chemical dissolution suggests itself. In principle, this is possible with the aid of an oxidizing acid or an acid plus oxidizing agent. Experiments of this type are known in connection with the investigation of yttrium barium cuprate superconductor powders which had been poured into copper tubes and compacted by deep drawing and rolling.

If, however, it is desired to proceed in the same manner in the case of bismuth-based superconductors, a strong attack of the acid on the superconductor or its precursor of the solidified melt is observed as soon as the copper casing is dissolved at one point and the surface of the solidified melt is laid bare. Specifically, it is found that the superconducting bismuth compounds are acid-soluble.

The object of the present invention is to provide a method which makes it possible to dissolve the copper casing without appreciably attacking the underlying superconductor or its precursor.

This object was achieved by adding sulfate ions to the solution containing the oxidizing acid or a nonoxidizing acid and an oxidizing agent. The principle underlying this invention is the formation of a protective layer, which suppresses a further attack of the acid upon the superconducting compound, composed of strontium sulfate and/or calcium sulfate from the sulfate added to the electrolyte and the alkaline earth metals contained in the superconducting compound.

In particular, the invention therefore relates to a process for producing molded bodies from precursors of oxidic high-temperature superconductors of the BSCCO type, which comprises treating a copper mold of the desired shape which encloses a solidified bismuth strontium calcium cuprate melt with a solution of a soluble compound containing sulfate anions, an aqueous mineral acid and an oxidizing agent until the copper mold is dissolved.

In addition, the process of the invention may preferably or optionally be one wherein

- a) the sulfates of sodium, potassium, ammonium, magnesium or zinc are used as soluble compound containing sulfate anions;
- b) hydrochloric acid or phosphoric acid is used as mineral acid;
- c) hydrogen peroxide or alkali chlorate is used as oxidizing agent;
- d) nitric acid is simultaneously used as aqueous mineral acid and oxidizing agent;
- e) sulfuric acid is simultaneously used as aqueous mineral acid and as compound containing sulfate anions;
- f) the copper mold is dissolved with a solution of aqueous nitric acid and sodium sulfate;
- g) the copper mold is dissolved with a solution of aqueous sulfuric acid and hydrogen peroxide;
- h) the treatment is carried out at 15° to 80° C.;
- i) a copper mold is treated which encloses the solidified bismuth strontium calcium cuprate melt and has one or more openings.

The amount of the compound containing sulfate anions to be used may be small per se and it is only necessary for the solubility product of calcium sulfate and strontium sulfate to be exceeded in the presence of min-

eral acid and oxidizing agent and at the selected temperature. Even 2 g of soluble sulfate compound, for example Na_2SO_4 , per liter of solution clearly exhibit the desired effects, but preferably concentrations of 100 to 300 g of soluble sulfate compound per liter of solution are employed.

The acid concentration, the treatment temperature and the treatment time are not crucial. In general, low acid concentration and low treatment temperature require a longer treatment time and vice versa. In other respects, the treatment time depends decisively on the thickness of the mold wall to be dissolved.

For example, 10 to 32% by weight HNO_3 , 10 to 20% by weight HCl or 10 to 35% by weight H_2SO_4 can be employed, but without being tied to these limits. The concentration of the oxidizing agent, for example of the hydrogen peroxide, plays a role to an equally small extent. It is only necessary to ensure that H_2O_2 is also constantly present in addition to the nonoxidizing mineral acid. H_2O_2 must therefore be gradually added, if necessary, in several portions.

It is, of course, within the scope of this invention if, in the case of somewhat thicker copper mold walls (for instance, above 0.5 mm), a larger proportion of the copper is dissolved, for example, in pure nitric acid and, if necessary, also at elevated temperature, but in the absence of sulfate ions and only then, when there is a danger of a local breakthrough of the superconductor surface, is a changeover made to the process according to the invention. In the absence of sulfate ions, the open end walls may be sealed, for example, with wax and thus be protected against the attack of the nitric acid. In this manner pure copper nitrate solutions are obtained which are not contaminated by sulfate. In addition, the copper mold is in total dissolved in a shorter time.

The process according to the invention is described in more detail below with reference to the embodiment using nitric acid:

The attack of nitric acid on the solidified supercon-

ductor of 7mm (surface: 3.86 cm^2), with the etching solution containing 10% by weight of nitric acid and 0 to 500 g.l⁻¹ sodium sulfate. The experiment was carried out at room temperature.

TABLE 1

Inhibitory action of sodium sulfate additions on the dissolution of BSCCO 2212 ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$) in nitric acid (10%)								
No.	Na_2SO_4 (anhydrous) $\text{g} \cdot \text{l}^{-1}$	Weight loss (%) after						
		5'	15'	30'	1 h	2 h	4 h	8 h
1	0	3.2	9.6	18.9	30.4	43.7	68.1	n.d.
2	100	0.1	0.15	0.23	0.32	0.39	0.50	0.65
3	200	0	0	0.02	0.15	0.32	0.76	1.42
4	300	0	0	0.04	0.12	0.26	0.45	0.90
5	400	0	0	0	0	0	0.04	0.16
6	500	0	0	0	0	0	0.03	0.08

n.d. = not determined

Adding sodium sulfate to 10% nitric acid does, however, also reduce the rate of dissolution of the copper:

TABLE 2

Dissolution of an empty copper tube piece having a comparable surface to that of BSCCO 2212 in Table 1 at various sodium sulfate concentrations				
No.	Na_2SO_4 (anhydrous) $\text{g} \cdot \text{l}^{-1}$	Weight loss (%) after		
		30'	2 h	8 h
1	0	0.3	3.8	11
2	100	0.1	0.6	3.3
3	200	0.04	0.26	1.7
4	300	0	0	0

With 10% nitric acid and 100 g of sodium sulfate, a substantial protection of the BSCCO core is already achieved, but the rates of dissolution of the copper are still very low for technical purposes. If 20% nitric acid is used, the conditions which are shown in Table 3 both for the dissolution of BSCCO and for that of copper (in brackets) are more favorable.

TABLE 3

Inhibitory action of sodium sulfate on the dissolution of BSCCO 2212 and copper (. . .) in 20% nitric acid at room temperature							
No.	Na_2SO_4 (anhydrous) $\text{g} \cdot \text{l}^{-1}$	Loss in weight (%) after					
		15'	30'	1 h	2 h	4 h	8 h
1	0	25(18)	44(34)	72(60)	100(100)	100(100)	100(100)
2	100	1.7(12)	2(23)	2.3(42)	2.5(87)	2.7(100)	3.0(100)
3	200	0.2(9)	0.2(18)	0.4(35)	0.7(74)	0.9(100)	1.3(100)
4	300	0(6)	0(13)	0(25)	0(52)	0.2(79)	0.2(100)
5	400	0(4)	0(9)	0(17)	0(31)	0(40)	0.2(52)
6	500	0(2)	0(4)	0(7)	0(9)	0(12)	0(18)

ductor melt depends, for a given nitric acid concentration and at room temperature, on the concentration of sulfate ions in the solution. Table 1 shows the losses in weight (in % of the initial weight) for a compact cylindrical test piece having a length of 14 mm and a diame-

The dissolution in 32% nitric acid at room temperature is shown in Table 4 (with the values for copper again in brackets):

TABLE 4

Inhibitory action of sodium sulfate on the dissolution of BSCCO 2212 and copper (. . .) in 32% nitric acid at room temperature					
No.	Na_2SO_4 (anhydrous) $\text{g} \cdot \text{l}^{-1}$	Loss in weight (%) after			
		15'	30'	1 h	4 h
1	100	0.51(71)	1.7(100)	4.4(100)	9(100)
2	<200+	0.13(38)	0(45)	0.12(59)	3(70)

+200 g of Na_2SO_4 are no longer completely soluble in 32% HNO_3 .

These experiments show that a combination of 20% nitric acid with 200 to 300 g of sodium sulfate are a sort of optimum with which a still usable rate of dissolution is accompanied by a good protective action. Of course, with continuous visual inspection, 32% nitric acid with 100 g of sodium sulfate is also suitable. However, copper dissolves much more slowly in a solution saturated with sodium sulfate because, with increasing dissolution of the copper, copper sulfate also crystallizes out immediately and readily deposits on the copper surface, inhibiting or rendering uneven the further dissolution.

Elevated temperature

The effect of elevated temperature was examined in 10% nitric acid:

TABLE 5

Inhibitory action of Na ₂ SO ₄ on the dissolution of BSCCO 2212 and copper in 10% nitric acid at 70° C. (values for copper in brackets)							
No.	Na ₂ SO ₄ (anhydrous)	Loss in weight (%) after					
	g · l ⁻¹	15'	30'	1 h	2 h	4 h	8 h
1	100	0.45(17)	0.77(32)	1.1(59)	1.4(100)	2.1(100)	2.9(100)
2	300	0(3)	0.16(7)	0.22(14)	0.5(27)	0.7(58)	0.7(92)
3	500	0(0)	0(0)	0(0)	—	—	—

Here again favorable results are obtained with 100 to 300 g of sodium sulfate in a liter. They are essentially equivalent to those which are obtained at room temperature with 20% nitric acid.

In principle, other solutions which have the same effect as nitric acid are also conceivable:

- Sulfuric acid + hydrogen peroxide
- Hydrochloric acid + hydrogen peroxide
- Hydrochloric acid + alkali chlorate

The suitability of the combination of sulfuric acid with an oxidizing agent is demonstrated using 20% sulfuric acid with 10% hydrogen peroxide at room temperature. In this case, the addition of a sulfate is not necessary since the sulfate anions needed are provided by the sulfuric acid itself.

TABLE 6

Differences in the dissolution of BSCCO 2212 and copper in 20% sulfuric acid with 10% H ₂ O ₂ added at room temperature					
Time:	5'	15'	1 h	2 h	4 h
Loss in weight of Cu/%	9.8	18	51	76	100
Loss in weight of BSCCO/%	0.2	0.4	0.55	0.75	1.02

EXAMPLE

Comparative Example

A copper tube having a length of 10 cm, a wall thickness of 1 mm and an internal width of 8 mm which contains a core composed of a solidified BSOCO high-temperature superconductor melt of the formula Bi₂Sr₂CaCu₂O_x, is placed in 20% nitric acid at room temperature and left there while stirring until the copper casing has been partially etched away (2.8 h) and a part of the core is exposed. The surface of the core exhibits deep holes and at the end faces, where the core was exposed to the action of the nitric acid without protection, it is dissolved away over a width of several mm.

EXAMPLE 2

Example 1 was repeated, but 300 g of sodium sulfate were dissolved in one liter of 20% nitric acid. After 3 hours no breakthrough of the core was as yet observable and a dense white film which covered the original surface had formed at the exposed end faces. After 12 hours, the copper had been dissolved down and the entire core was then covered with the white thin covering layer. Signs of an uneven removal or pitting were not observed.

EXAMPLE 3

A similar rod to that in Example 1 was brought into contact with 200 ml of 20% sulfuric acid to which 30 ml

of 10% by weight hydrogen peroxide, divided into three equal portions, was gradually added, in which process copper was dissolved. The solution was stirred by means of a magnetic stirrer and the temperature was 25° C. After 15 hours of contact the copper casing had been dissolved. The superconductor core exhibited no acid attack on its surface, which was uniformly covered with alkaline earth metal sulfate.

We claim:

1. A process for removing a copper mold from a molded high-temperature superconductor precursor body which comprises treating a copper mold which encloses a molded body of solidified bismuth strontium calcium cuprate melt with a solution of (a) a compound containing sulfate anions, (b) an aqueous mineral acid and (c) an oxidizing agent, to dissolve the copper mold and to form a protective layer of at least one of strontium sulfate or calcium sulfate on said molded body from the sulfate anions and strontium and calcium contained in the solidified melt, said protective layer suppressing an attack of the mineral acid upon said molded body, wherein

- (1) said compound containing sulfate anions is a sulfate of sodium, potassium, ammonium, magnesium or zinc; and
- (2) either hydrochloric or phosphoric acid is used as said mineral acid in combination with said compound containing sulfate anions and said oxidizing agent, or nitric acid is simultaneously used as said mineral acid and said oxidizing agent in combination with said compound containing sulfate anions.

2. A process as claimed in claim 1, wherein hydrogen peroxide or alkali chlorate is used as said oxidizing agent.

3. A process as claimed in claim 1, wherein the copper mold is dissolved with a solution of aqueous nitric acid and sodium sulfate.

4. A process as claimed in claim 1, wherein the treatment is carried out at 15° to 80° C.

5. A process as claimed in claim 1, wherein said copper mold has one or more openings and encloses the solidified bismuth strontium calcium cuprate melt.

* * * * *

United States Patent [19]

Kukanskis et al.

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[45] Date of Patent: Aug. 6, 1991

[54] COMPOSITION AND METHOD FOR
IMPROVING ADHESION OF COATINGS TO
COPPER SURFACES

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156/656; 156/666; 252/79.1; 252/79.4

[58] Field of Search 134/3, 41; 156/656,
156/666; 252/79.1, 79.4

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[57] ABSTRACT

A composition for cleaning and improving the adhesion characteristics of a copper surface (which is in turn adhered to an underlying substrate) so as to enable a coating, e.g., of photoresist, to be adhered easily and completely to the copper surface, the cleaning and adhesion promoting composition consisting essentially of an aqueous solution of an alkane sulfonic acid, a surfactant and an oxidizing agent of a type, and present in an amount, sufficient to provide controlled conversion of the copper surface to a substantially clean, micro-roughened surface, without removing the copper surface from the underlying substrate, so that the adhesion characteristics of the copper surface are substantially increased for receiving and securely adhering a subsequently applied coating.

11 Claims, 2 Drawing Sheets



FIG. 1

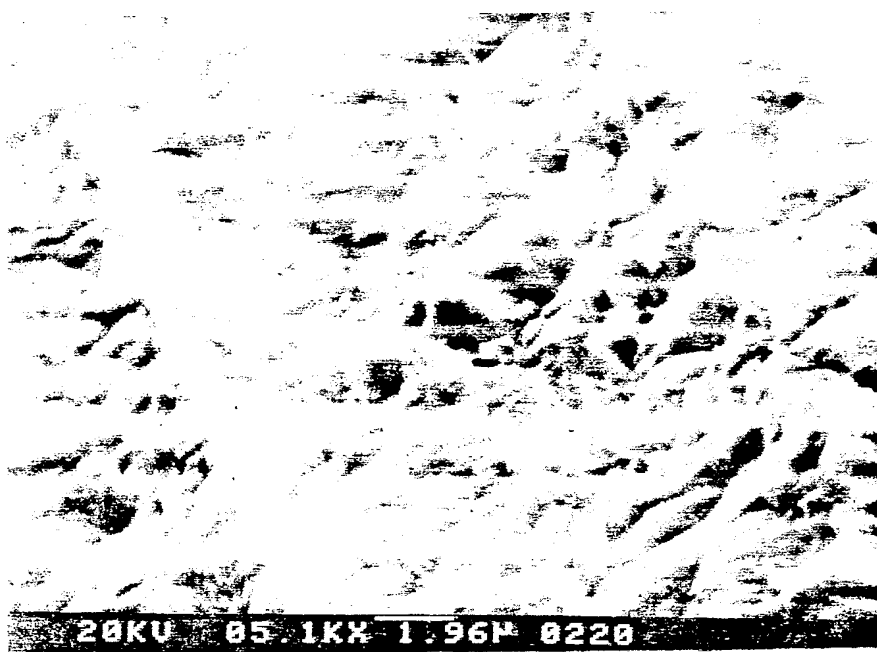


FIG. 2

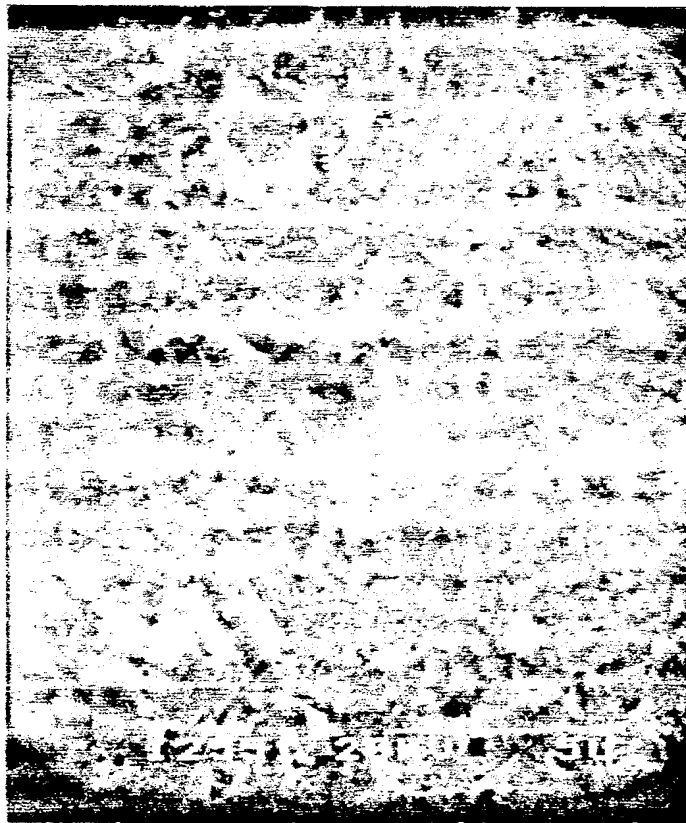


FIG. 3

COMPOSITION AND METHOD FOR IMPROVING ADHESION OF COATINGS TO COPPER SURFACES

BACKGROUND OF THE INVENTION

The present invention relates to improving the adhesion characteristics of a copper surface to enable subsequently applied coatings to be completely and easily adhered to the copper surface and, more particularly, to an improved cleaning and adhesion promoter composition and method for treating the surface of copper foil laminates used in printed circuits to improve the adhesion of subsequently applied coatings affixed to the copper surface.

The composition of the invention removes contaminants from the copper surface (which in turn is adhered to an underlying substrate) and enhances the surface topography thereof by controlled conversion of the copper surface from a relatively smooth surface to a micro-roughened surface, through a microetching which removes, e.g., from about 0.5 to 5 microns of the copper. In this way, a copper foil laminate for use as a printed circuit board is provided with improved adhesion characteristics to enable subsequently applied photoresist or oxide coatings to more easily and completely adhere to the copper surface. More particularly, the invention relates to an improved cleaning and adhesion promoter composition which is capable of concurrently bringing about both cleaning and microetching of the copper surface to improve the adhesion characteristics of the copper surface prior to the application of photoresist or oxide coatings to the copper surface in the manufacture of printed circuit boards.

In a typical preparation of printed circuits, a copper foil is bonded to an insulating substrate which may be phenolic, epoxy, polyimide, polyester, or the like. The foil is normally treated electrolytically to provide a specific surface structure, such as disclosed in U.S. Pat. Nos. 3,293,109; 3,318,758; 3,518,168; 4,049,481; 4,131,517; 4,176,035; and others.

Multilayer printed circuit boards are assemblies containing several copper foil-clad substrate inner-layers, further bonded to each other through layers of semi-cured polymeric material, which are subsequently cured at elevated temperatures and pressures to form the complete laminate assembly. Prior to this assembly, the copper foil of the innerlayers is imaged and etched to form the innerlayer circuits of the assembly.

The printed circuit board industry is continuously faced with an increasing demand for higher density circuitry. This has led to the production of finer lines of circuitry and is leading toward the use of thinner and thinner copper foils. As this trend continues, the preparation of the innerlayer copper foil becomes increasingly more critical. The use of thinner foils requires much tighter processing controls in order to produce uniform circuitry.

Combining the steps of initially cleaning and preparing a copper surface adhered to an underlying substrate to improve the adhesion characteristics of the copper surface for easily and completely affixing subsequently applied coatings would reduce the labor involved as well as the time to process the circuit boards. Thus, the final cost of manufacturing each board would be reduced.

While the present invention is particularly apropos of printed circuit board manufacture, and more particu-

larly innerlayers of multilayered circuit boards, the need to remove contaminants from copper surfaces and to improve the adhesion characteristics of copper surfaces so that subsequently applied coatings will be more completely adhered to the copper surface also arises in other contexts where a contaminant-free surface with adhesion-improved characteristics of the copper surface is needed for subsequent plating operations for decorative or functional purposes.

PRIOR ART

Preparing copper innerlayer laminates previously involved several process steps to ensure a clean copper foil surface prior to application of photoresist and/or oxide coatings. The processes used in industry include a pumice or mechanical scrub usually followed by a chemical treatment of peroxide/sulfuric, or persulfate. Such processes have their own inherent problems: for example, when pumice is used there is pumice entrapment in the copper foil, or in the case of mechanical scrubbing with nylon brushes, gouging of the foil surfaces results. In addition, thinner innerlayer materials are susceptible to other defects and damage from aggressive mechanical surface scrubbing, such as distortion and incomplete treatment of copper surfaces due to worn scrubbers or plugged nozzles. The subsequent chemical treatment cannot overcome the damage done to the foil by these mechanical methods. Also, the regular chemical treatments are not effective in removing the chromate films on the foil that may remain after scrubbing, thereby resulting in a poor surface topography for the adhesion of the subsequently applied photoresist and/or oxide coatings.

In order to avoid some of the damaging effects of scrubbing, some manufacturers use a chemical cleaning method. In this instance the laminate is processed in an alkaline or acid cleaner traditionally known in the art, followed by a conventional chemical treatment (e.g., peroxide/sulfuric acid as above noted). The cleaners have the ability to remove the handling soils, fingerprints and oils that may be present on the laminate, but usually have little effect on the chromate film on the copper foils present from the lamination process. Again, the chemical treatment only partially removes the chromate film on the copper surface which in turn produces a less than satisfactory application of the subsequently applied photoresist or oxide coating because it does not adhere properly to the copper surface at the places where the chromate film residue remains.

SUMMARY OF THE INVENTION

A primary object of the present invention is to provide a composition useful for treating a copper surface, adhered to an underlying substrate, by removing contaminants from the copper surface and improving the adhesion characteristics of the copper surface to enable subsequently applied coatings to be more easily and completely adhered to the copper surface.

Another object of the invention is to provide a composition for concurrently removing contaminants from a copper surface, adhered on an underlying substrate, and for enhancing the surface topography of the copper surface of the laminate by controlled conversion of the substantially smooth copper surface to a substantially micro-roughened topography, thereby improving the adhesion characteristics of the copper surface for subsequently applied coatings.

Yet another object of the invention is to provide a composition for removing contaminants such as chromate and/or triazole tarnish inhibitor films as well as handling soils from a copper surface while concurrently treating the topography of the copper surface to achieve enhanced adhesion characteristics of the copper surface so that subsequently applied photoresist or oxide coatings are completely adhered to the copper surface.

Still another object of the invention is the provision of a composition of the type described which effects, in a single application step, the removal of contaminants from a copper surface and roughens the surface topography of the copper surface to provide better adhesion characteristics of the copper surface to insure that subsequently applied photoresist or oxide coatings are completely adhered to the copper surface.

Another object of the invention is the provision of a cleaning and adhesion promoter composition of the type described which can be applied by the techniques of immersion or spraying, and which employs ingredients that are environmentally sound.

These and other objects are achieved by the provision in the present invention of a composition and method for treating a copper surface, which is in turn adhered to an underlying substrate, the composition consisting essentially of an aqueous solution of an alkane sulfonic acid, a surfactant, and an oxidizing agent of a type, and present in an amount, to provide in cooperating interaction with the surfactant a cleaning of the copper surface and a controlled conversion of the copper surface from a substantially smooth surface to a substantially micro-roughened surface topography so that the copper surface has increased adhesion characteristics for coatings subsequently applied to the copper surface and without removing said copper surface from the underlying substrate. In the preferred embodiment, the composition consists essentially of between about 5% and 60% by weight of the alkane sulfonic acid, between about 0.01% and 50% by weight of the oxidizer, and between about 0.001% and 10% by weight of the surfactant.

In the preferred embodiment of the invention, the alkane sulfonic acid comprises methane sulfonic acid, the oxidizer comprises ferric nitrate, and the surfactant comprises a nonionic and/or anionic surfactant.

The foregoing composition is effective not only in removing soils and the like (e.g., the chromate and/or triazole tarnish inhibitor films present on copper foil-clad substrates by reason of the copper foil lamination process), but concurrently also in roughening the surface by converting the substantially smooth copper surface to a substantially uniformly micro-roughened copper surface by means of a microetching of from about 0.5 to 5 microns of the copper thickness to enhance the adhesion characteristics of the copper surface for the subsequent application thereto of coatings such as photoresist or oxide coatings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an electron-microscope-generated photograph showing the surface of copper foil before being treated by the cleaning adhesion promoter composition at a magnification of 5000 \times and at a 45° angle to surface to show the surface topography;

FIG. 2 is an electron-microscope-generated photograph at the same magnification and at a 45° angle to surface as FIG. 1, showing the surface topography of

copper foil after being treated by the method of this invention as set forth in Example 1; and

FIG. 3 is an electron-microscope-generated photograph at a magnification of 4500 \times and at a 45° angle to surface showing the surface topography of copper foil treated by a prior art method according to Example 3 of U.S. Pat. No. 4,632,727.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, a combination cleaner and adhesion promoter composition is provided to act as a pretreatment for a copper surface adhered to an underlying substrate so as to remove contaminants such as soils, fingerprints, triazole tarnish inhibitor and chromate films from the surface of the copper and to provide improved surface topography on the copper surface which will improve the bonding of any subsequently applied photoresists (i.e., both liquid or dry-film type) or oxide coatings to the copper surface.

This cleaning and adhesion promoting composition performs two functions simultaneously when applied to the copper surface adhered to an underlying substrate. First it cleans the copper surface being treated by removing any contaminants on the surface, such as for example soils, fingerprints, triazole tarnish inhibitor, chromate films, and the like. Then, it converts the substantially smooth copper surface through a controlled reaction to a substantially uniformed micro-roughened surface topography to thereby further improve the bonding adhesion characteristics of the treated copper surface to enable subsequently coatings to be easily and completely adhered to the copper surface. Examples of subsequently applied coatings used in the manufacturing of printed circuit boards are photoresists (i.e. both liquid or dry film type) and/or oxide coatings. A copper foil laminate is but one example of a copper surface that may be so treated by this cleaning and adhesion promoting composition.

The cleaner/adhesion promoter is composed of water, alkane sulfonic acid (generally either methane or ethane sulfonic acid), an oxidizing agent for copper, and specific surfactants. The alkane sulfonic acid is used from about 5% to about 60% by weight of the composition, preferably from about 15% to about 40% by weight. The oxidizer can range from about 0.1% to about 50% by weight of the composition, preferably from about 1% to about 15% by weight, and most preferably from about 5% to about 10% by weight, all of course depending upon the type of oxidizing agent employed. The oxidizers can include ferric nitrate, peroxide, ferric chloride, and copper chloride, with ferric nitrate preferred. The surfactants range from about 0.001% to about 10% by weight of the composition, preferably from about 0.01% to about 3% by weight. The surfactants alone or in combination, preferably encompass nonionic and anionic surfactants. Examples of nonionic surfactants include without limitation: ethoxylated nonyl- and octylphenols of ethylene oxide from 3 to 30 moles of ethylene oxide, preferably 3.5 moles, and modified polyethoxylated straight chain alcohols as are available under tradename Triton DF-16 from Rohm & Haas; alkyl polyoxyalkylene ether, e.g. Mazawet DF from Mazer Chemical; and block copolymers of ethylene oxide and propylene oxide such as Pluronic 31R1 from BASF. Anionic surfactants include without limitation: sulfonated aryl and alkyl hydrocar-

bons such as Petro BA from Desoto, Inc.; sulfated aryl and alkyl hydrocarbons such as Sipon BOS from Alcolac, Inc.; and phosphate esters such as Triton H-66 from Rohm & Haas.

The cleaner/adhesion promoter composition is generally used at a temperature ranging from about ambient to about 130° F. with a preferable range being from 80° F. to 95° F., from a contact time of from about 10 seconds to 10 minutes, preferably from 30 seconds to 5 minutes. When the composition is used with peroxide, ferric chloride or copper chloride as the oxidizer, these materials are consumed in the reaction which remove copper from the copper surface. Thus, using these compounds necessitates regular additions of the oxidizers to maintain continuous operation. When ferric nitrate is used, the oxidizer is lost only by drag-out. It is theorized that upon reacting and removing copper from the copper surface, the iron is re-oxidized from ferrous to ferric and is available to again remove more copper. Thus, the only limiting factor in the cleaner/adhesion promoter in this regard is its capacity to hold copper in solution.

The oxidizer must be of a type, and present in an amount, sufficient to provide in cooperating interaction with the surfactant, a controlled conversion of the copper surface from a substantially smooth surface to a substantially clean, substantially uniformly micro-roughened surface, so that the bonding characteristics of the copper surface are substantially increased for securely adhering a subsequently applied coating to the copper surface, without at the same time removing the copper surface itself from the underlying substrate to which it is adhered. An oxidizing agent which is too active, and/or which is used in too substantial concentrations, not only runs the risk of uncontrolled stripping of the copper surface from its underlying substrate, but more importantly has been found ineffective to produce the required micro-roughened topography on the remaining copper surface. Results such as this have been found with compositions containing nitric acid as the oxidizer. Even where complete stripping is avoided, the remaining copper surface is nevertheless surprisingly smooth and unacceptable for promoting adhesion of subsequently applied coatings.

The cooperating interaction of a suitable oxidizer, used in suitable amount, along with the surfactant, provides a controlled cleaning and conversion of the substantially smooth copper surface to a substantially micro-roughened, clean surface, with between about 0.5 and 5 microns of the original copper surface being removed. This micro-roughening provides increased surface area, thereby improving the bonding characteristics of the treated copper surface, especially to subsequently applied coatings.

The alkane sulfonic acid in the cleaner/adhesion promoter composition according to the present invention is selected from any one or more compounds having the formula RSO_3H , where R is a lower alkyl group having from 1 to 5 carbon atoms, and preferably 1 or 2 carbon atoms, i.e., methane sulfonic acid or ethane sulfonic acid, with methane sulfonic acid most preferred.

The amount of alkane sulfonic acid employed in the aqueous compositions is preferably in an amount ranging from 3% to 45% by volume, more typically 10% to 40% by volume, and most typically 25% to 30% by volume, based upon a 70% methane sulfonic acid aqueous solution, which is a form in which methane sulfonic acid is commonly sold. Obviously, however, other con-

centrations, and the anhydrous form of the acid, can be used in making up the composition.

The present invention also affords a means for regenerating the bath per se or any removed portion thereof both to recover metal values and to reestablish operating concentrations of the alkane sulfonic acid.

BEST MODE

As indicated earlier, the composition of the invention provides for the removal of contaminants, such as dirt, soils and chromate and thiazole tarnish inhibitors, from the copper surface and provides a fine uniform etch with good topography to enhance photoresist or oxide adhesion to the surface of the copper. For one ounce copper-clad innerlayers (.0014 inches of copper), best results occur when the composition effects removal of from between 0.5 microns (0.00001 in) to 5 microns (0.0002 in) of the copper. The composition may be applied by immersion, spraying or other modes.

Not only are the contaminants removed from the surface of the copper foil but the copper surface topography itself undergoes a change—that is, the substantially smooth surface is micro-roughened by a controlled conversion to a substantially clean, substantially uniformly roughened surface topography. Compare FIGS. 1 and 2. Note that in FIG. 2 the number and magnitude of the irregularities on the copper surface is increased using the composition of the invention. Such action increases the surface area of the copper available for bonding and thus promotes better adhesion to the copper surface of a subsequently applied coating.

The following examples will further illustrate the best mode of operation.

EXAMPLE 1

A 7 mil core, 1 oz. copper laminated epoxy innerlayer was processed through an immersion cleaner/micro-etch prior to dry-film photoresist lamination. The process using the steps set forth below was as follows:

- (1) Cleaner/adhesion promoter, for 3 minutes at 95° F.
- (2) Two cold water rinses
- (3) Hot water rinse
- (4) Hot air dry
- (5) Dry-film lamination
- (6) Image
- (7) Develop
- (8) Alkaline etch - Ultra Etch FL for 45 seconds at 120° F.
- (9) Cold water rinse
- (10) Dry

The cleaner/adhesion promoter used in step (1) above contained the following:

Water	57.325% by weight
Methane Sulfonic Acid (70%)	35.0% by weight
Ferric Nitrate	7.5% by weight
Mazawet DF	0.05% by weight
Triton DF-16	0.075% by weight
Petro BA	0.05% by weight

The amount of copper removed was approximately 1.25 microns (0.00005 inches) from the copper foil surface.

Upon inspection after the alkaline etching of the 1 oz. of copper in non-resist areas to define the innerlayer circuitry, no lifting of the photoresist was evident. The surface of the foil before and after treatment with the

cleaner/micro-etch is shown in the electron-microscope-generated photographs labeled FIGS. 1 and 2, respectively. The micro-roughened surface with numerous deep irregularities and an average vertical depth penetration of 1.25 microns is shown in FIG. 2 as contrasted with the untreated copper surface of FIG. 1 which is substantially smooth and has a relatively even and unbroken copper surface topography.

EXAMPLE 2

The same process as used in Example 1 was utilized and repeated except that the cleaner/adhesion formulation was as follows (i.e., no surfactants were employed):

Water	57.5% by weight
Methane Sulfonic Acid 70%	35.0% by weight
Ferric Nitrate	7.5% by weight

Inspection of the laminate prior to dry-film lamination showed a splotchy copper surface indicative of unevenness of the surface topography. Inspection after dry-film and alkaline etch revealed an undesirable lifting of the dry-film in areas corresponding to the location of the splotchy areas on the copper foil surface.

EXAMPLE 3 (PRIOR ART)

The process as used in Example 1 was repeated, but the etchant solution used was that described by Nelson in his U.S. Pat. No. 4,632,727 (Example 3) having the following formulation:

Distilled Water	1100 cc
Methane Sulfonic Acid 70%	1000 cc
Nitric Acid 70%	900 cc
Reten 520 (2% solution)	100 cc
(A Hercules Polyacrylamide)	
Varion H.C.	5 cc
(A Sherex Chemical Surfactant)	

This etchant solution was used at 95° F. (approx. 34° C.) versus 45° C. as indicated in the Nelson patent. The time of etching was reduced to 24 seconds. The action of this composition was very aggressive, but did not provide a proper topography of the copper surface. FIG. 3 shows the unacceptable smooth topography resulting from this treatment, while FIG. 2 shows the preferred enhanced substantially micro-roughened surface topography resulting from the application of the cleaner/adhesion promoter composition of the invention.

The above description is for the purpose of teaching a person of ordinary skill in the art how to practice the invention. This description is not intended to detail all of the obvious modifications and variations of the invention that will become apparent to the skilled worker upon reading. However, it is intended that all such modifications and variations be included within the scope of the invention which is defined by the following claims.

We claim:

1. A process for cleaning and improving the adhesion characteristics of a copper surface, adhered to an underlying substrate, for enabling a subsequently applied coating to be easily and completely adhered to the copper surface, said process comprising contacting said copper surface with a composition consisting essentially of water, an alkane sulfonic acid, a surfactant, and an

oxidizing agent for copper, said oxidizing agent being of a type, and present in an amount, sufficient to provide, in cooperating interaction with the surfactant, and under the conditions and time of said contacting, controlled conversion of the copper surface to a substantially clean, substantially uniformly micro-roughened surface without etching said copper surface from said underlying substrate, whereby the adhesion characteristics of said copper surface are substantially increased for receiving and securely adhering a subsequently applied coating thereto.

2. The process according to claim 1, wherein said alkane sulfonic acid is present in an amount of from about 5% to 60% by weight; said oxidizer is present in an amount of from about 0.1% to 60% by weight; and said surfactant is present in an amount of from about 0.001% and 10% by weight.

3. The process according to claim 2 wherein said surfactant is a mixture of nonionic and anionic surfactants.

4. The process according to claim 1, wherein said nonionic surfactant is selected from the group consisting of ethoxylated nonylphenols and octylphenols and alcohols of ethylene oxide, alkyl polyoxyalkylene ether, and block copolymers of ethylene and propylene oxide; and the anionic surfactant is selected from the group consisting of sulfonated aryl and alkyl hydrocarbons, sulfated aryl and alkyl hydrocarbons, and phosphate esters.

5. A process for cleaning and improving the adhesion characteristics of a copper surface adhered to an underlying substrate, for enabling a subsequently applied coating to be easily and completely adhered to the copper surface, said process comprising, contacting said copper surface with a composition consisting essentially of water, methane sulfonic acid, ferric nitrate, and a surfactant mixture of ethoxylated nonyl- and octylphenols and alcohols of ethylene oxide, alkyl polyoxyalkylene ether, and sulfonated aryl and alkyl hydrocarbons, for a time and at conditions effective to provide a controlled conversion of the copper surface to a substantially clean, substantially uniformly micro-roughened surface topography without removing said copper surface from said underlying substrate.

6. A process according to claim 5 wherein said composition consists essentially of water, between about 15%-40% by weight of an alkane sulfonic acid selected from the group consisting of methane sulfonic acid and ethane sulfonic acid; between about 1%-15% by weight of an oxidizer selected from the group consisting of ferric nitrate, peroxide, ferric chloride, and copper chloride; and between about 0.01%-3% by weight of a surfactant selected from the group consisting of non-ionic surfactants and anionic surfactants, and mixtures thereof.

7. A process according to claim 6 wherein said composition consists essentially of water, about 35% by weight of an methane sulfonic acid (70%), about 7.5% by weight of ferric nitrate, and about 1.75% by weight of a surfactant mixture of ethoxylated nonyl- and octylphenols and alcohols of ethylene oxide, alkyl polyoxyalkylene ether, and sulfonated aryl and alkyl hydrocarbons.

8. The process according to claim 3 wherein said step of contacting said surface with said composition is achieved by immersing said copper surface in said composition.

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9. The process according to claim 3 wherein said step of contacting said surface with said composition is achieved by spraying said composition onto said copper surface.

10. The process according to claim 3 wherein said

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copper surface is a copper-clad printed circuit board substrate.

11. The process according to claim 10 wherein said subsequently applied coating is selected from the group consisting of photoresist and oxide coatings.

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